PHOTOGRAPHIC SCIENCE and TECHNIQUE

MAY 1955

Series II, Vol. 2, No. 2

IN THIS ISSUE

MATERIALS FOR SCIENTIFIC PHOTOGRAPHY

In Paid Advertisements, the Industrial Photographic Division of the Eastman Kodak Company, Rochester 4, New York, has announced their willingness to save time and stationery for the scientist and for themselves through the medium of a booklet that summarizes the facts about various materials, familiar and obscure, which they market for scientific photography. No doubt professional photographers involved in scientific photography can get a copy too.

The booklet describes Kodak offerings in the following categories: 1) for general photography and photomicrography, 2) for the specialized recording of radiation, 3) for general spectro-chemistry, 4) for the deep ultraviolet, 5) for the infrared, 6) for autoradiography and nuclear particle tracks, 7) for electron imagery, 8) for the finest image detail, 9) for modifying spectral distribution, 10) for attenuating light, 11) for other photographic techniques. Ask for "Kodak Photographic Materials and Light Filters for the Laboratory".

Another recent Kodak publication of interest to the technical photographer, but this one costs fifty cents a copy, is "Use, Maintenance, and Repair of Professional Equipment", a Kodak Professional Data Book. This is a companion to three others that comprise the Kodak Professional Handbook: "Professional Printing," "Negative Making," and "Camera Technique".

MAGNETIC SOUND TRACK APPLICATOR

Narration, Music, or Sound effects can be added to old 16mm films after they have been furnished with magnetic sound tracks. New films, singly or doubly perforated, can also be furnished with magnetic tracks, in any one of three precise widths, by the striping machine recently introduced by Reeves Soundcraft Corporation of New York City.

Lacquer is applied to the film. Iron oxide particles adhere to the wet lacquer. The film then passes into an electrically heated drying chamber in the base of the machine. The explosive vapors produced as the solvents leave the lacquer

are protected from contact with arcs or sparks by Crouse-Hinds (Syracuse, New York) explosion-proof electrical conduit components with flame-tight joints.

Crouse-Hinds junction boxes protect heater terminal connections on this film sound stripping machine. The start-stop contactor below and the three-station pushbutton switch for the reel feed, above right, also are explosion-proof units.

DEIONIZED WATER SUPPLY

Deionized water comparable to triple distilled water for use in their laboratories is now available to photographers in convenient quantities at low cost with two new devices announced recently by Central Scientific Company, 1700 Irving Park Road, Chicago.

Color photographers and others requiring a great deal of deionized water will be served by the Quikpure Constant Flow Demineralizer unit which can be hooked up to the tap water supply. From 10 grain tap water this unit is capable of producing automatically about 600 gallons of deionized water at a cost of about 4 cents per gallon, or less. Regular distilled water sells for around 40 cents per gallon.

The demineralizer unit contains a polyethylene bottle charged with 30 pounds of anion and cation resins housed in an attractive metal cabinet. The water is drawn as desired from a

---

gooseneck spout. A warning light on the cabinet indicates when the bottle needs recharging. This unit is priced at $295, f.o.b. Chicago. A replacement charge of 30 pounds of resins is $25 on an exchange basis.

The other Quikpure device consists of either a pint or quart size polyethylene squeeze bottle which contains the mixture of the cation and anion resins. Tap water poured into the bottle comes into immediate contact with the resins and is demineralized in about one minute. A specially designed cap permits the user to discharge the water from the bottle without letting the resins escape. When the resins cease to react, a color change occurs.

The quart bottle has a minimum removal capacity of 210 grains and the pint 70 grains. In both cases, the number of gallons depends upon the hardness of the water. Deionized water made with Quikpure bottles costs about 10 cents per gallon. The quart Quikpure is priced at $5.95 with refills listing at $3.50 each. The pint size sells for $2.50 with one set of three refills at $4.50 per set.

TECHNIQUE FOR PROFESSIONALS

COLLECTING AND PUBLISHING ADVICE on technical problems of the professional photographer is one of the aims of this publication. A reader seeks advice on the preparation of glossy print surfaces, hardened by a heated high-gloss drum, so that they will accept retouching liquids.

Use of wetting agents in the water used with retouching pigments has been mentioned, but nobody seems to have actually tried it. If this is a problem you have solved, write the editor describing your methods for the benefit of other readers.

BOSTON UNIVERSITY ANNOUNCES RESEARCH ASSISTANTSHIPS IN THE INSTITUTE OF AIR PHOTOGRAPHY

THE BOSTON UNIVERSITY GRADUATE SCHOOL has recently announced the availability of Research Assistantships to candidates for a Master's Degree in Air Photography. This is a professional graduate program designed to provide instruction in optics, photography, electronics and photographic interpretation directed toward the applications and research problems of air photography.*

The increasing use of air photography in our society and the opportunities it offers as a research tool and as a field of research in itself have warranted the establishment of the Institute of Air Photography to provide:

(a) a program designed for the users of this medium;
(b) research facilities and an experienced staff for the development of new concepts and techniques for air photography;
(c) a place for the evaluation of concepts, techniques, and instrumentation in terms of their effectiveness;
(d) use of photography as a tool of research in geographic and geologic exploration.

The curriculum of the Boston University Institute of Air Photography has been designed to provide maximum flexibility depending on the student's background and interests. The basic course of this program, "Air Photography," reviews the entire air photographic system with particular mention of both the technical problems involved as well as its applications.

* Macdonald, D. E., "Air Photography," JOSA, Vol. 43, p. 290 (1953).

This basic course is supplemented within the scope of the technical problem with pertinent courses in optics, photography and electronics. The applications of air photography are further discussed in additional courses in photographic interpretation, cartography and photogrammetry. Optional courses in physics, geography and psychology provide for additional breadth or specialization.

Individual student research activities are conducted in directed study and research courses under the immediate supervision of the staff of the Boston University Physical Research Laboratories. Current research activities include: geometrical optics, physical optics, the application of communication and information theory to optics, aerial photography, photographic physics, electronics (particularly as applied to optics and the study of image-forming devices) and psycho-physics (vision, photographic interpretation). Finally, the students are kept informed of the latest researches, developments, and operations in the field of air photography in a weekly seminar. Two years of course work, including a thesis, are necessary to complete the degree requirements.

Research Assistantships carry stipends of $1200 and up per academic year. Assistants pay their own tuition and spend about twenty hours per week on research projects in air photography in the Physical Research Laboratories. Summer employment is normally offered to Assistants to provide continuity in their program of research.

Application blanks for admission to the Graduate School and for Research Assistantships can be obtained from the Office of the Graduate School, Boston University, 725 Commonwealth Avenue, Boston 15, Massachusetts. Applications should be submitted as soon as possible. Further information can be obtained from Mr. R. L. Dussault of the Physical Research Laboratories.

INFORMATION AGENCY PICTURE FILE

The Press Service of the U. S. Information Agency in Washington, D. C., has a collection of more than 50,000 photographs specializing in a broad picture of America and its way of life. Subjects range from atomic research to children rolling eggs on the White House lawn.

The Press Service Photographic Library is a central pool of picture material used in a variety of ways by the Agency in telling the American Story abroad. They are the illustrative basis for newspaper and magazine articles, booklets, pamphlets, displays and posters which the agency sends to 200 field posts in 77 countries.

The present file has been built up from photographic sources in the United States. Pictures are obtained from government agencies, industrial concerns, commercial news syndicates, picture firms and individuals. In addition, IPS staff photographers provide their own documentation of America and furnish pictures on current news.

Among the fields covered are scenic views of the United States, social institutions (colleges, hospitals, churches), industry, agriculture, local customs, scientific discoveries, fashions, and significant figures in American life, both in the news and of historical importance.

The Library at first contained Americana almost exclusively, but it has now turned to documentation of U. S. activities in other countries. These include the technical assistance and military assistance programs and photographs now being acquired from the Agency's field posts.

ON THE MINIMUM ENERGY DETECTABLE
BY PHOTOGRAPHIC NEGATIVES

R. Clark Jones*

ABSTRACT

It is awkward to define the minimum energy that can be detected by visual inspection of a photographic film, because the question is a psychophysical concept, and because the reliability of the detection must be specified before the definition is complete. The "noise equivalent energy," however, is more easily defined, being a purely physical quantity. Psychophysical tests indicate that the latter is roughly one-fifth of the former.

It is well known that pre-exposing a film often increases its ability to photograph dim objects successfully. It is shown that the use of a pre-exposure is successful also in reducing the noise equivalent energy. Whether or not the film is pre-exposed, the developed film shows the phenomenon of granularity: the density varies from one region of the film to another. Let the density be measured by a photoelectric densitometer whose aperture has the area A, and let ΔD be the root-mean-square deviation of the various measured densities from the mean value of the measured densities.

Then the noise equivalent energy K_N is defined as the amount of radiant energy which, upon striking the pre-exposed and undeveloped film uniformly over a region of area A, will increase the average density of the region by just ΔD. It is shown that K_N varies approximately as $A^{1/2}$.

On the basis of data made available by the Eastman Kodak Company, K_N has been determined for four different films, as a function of (1) the area A, (2) the wavelength of the incident radiation, and (3) the amount of pre-exposure. A somewhat more useful quantity is the figure of merit M_2 for Type II detectors, defined by $M_2 = 3 \times 10^{-8} A^{1/2}/K_N$, where A is expressed in square microns, and where K_N is in ergs. For a radiation wavelength of 0.42 micron, and for the optimum pre-exposure, values of the figure of merit were found for four films:

The optimum pre-exposure for the four films is found empirically to be equal to the exposure for which, the gradient of the characteristic curve is equal to 0.3 times the maximum gradient.

For a negative material with a figure of merit M_2 equal to 200, and for a sensitive area A of 160 square microns, one has $K_N = 1.9 \times 10^{-8}$ erg, or 400 photons of wavelength 0.42 micron.

EXPERIMENTAL PHYSICISTS have long realized that in order to detect a very small amount of light by photographic means, it is necessary to use a very sensitive film, to employ optimum methods of development, and to appraise the film with the aid of a precise densitometer, preferably (sometimes *necessarily*) of the photoelectric type.

Recognizing this, and asking, "What is the smallest amount of light that can be detected photographically?" immediately poses the more basic question, "What prevents one from detecting an arbitrarily small increment of density in the exposed film, and thereby detecting an arbitrarily small amount of light?"

The lower limit on the density change that can be detected is set by the variation in the density from one region to another of an unexposed or of a "uniformly exposed" film. In the language of the communication engineer, this density fluctuation constitutes the *noise* of the system. The finite amplitude of this fluctuation requires that a finite change in density be produced in order that the change be a reliable indication of a change in the exposure of the film.

The density fluctuation existing in a photograph causes the subjective impression of *graininess*. The magnitude of the density fluctuation, as determined by purely physical measurements, is called the *granularity* of the negative. The relation between the graininess and the granularity of photographic materials has been the subject of an excellent series of papers[1-8] by L. A. Jones and G. C. Higgins of the Eastman Kodak Company.

Experimental physicists have also found that the sensitivity of films used in photographing dim objects can often be increased substantially by pre-exposing the film to an unfocused source of light. This procedure, although causing some increase in the magnitude of the density fluctuation, may increase even more the change of density for a given subsequent exposure. The exposure subsequent to the pre-exposure will hereafter be called simply the exposure.

It is supposed in this paper that the film is given a uniform pre-exposure of arbitrary amount. It will be shown in Part IV that the minimum detectable energy has its smallest value for a pre-exposure that is sufficient to bring the density of the developed film up to a value that is roughly 0.1 or 0.2 unit above the density of the film base.

Actually, the present paper does not discuss the minimum detectable energy as such. The minimum detectable stimulus is a concept that has found extensive use in many fields of science, but it suffers from two limitations that are not basic to the problem at hand. First, the concept often implies the direct use of a sense organ, which fact makes the minimum detectable energy a psychophysical concept rather than a purely physical concept. Second, the concept entails specifying in advance how reliable the "detection" must be.

This paper deals with a comparable but in many respects more simple concept, which is called here the "noise equivalent energy", in accordance with the terminology used in other branches of science. As will be seen, this concept is purely physical and thus avoids the two limitations mentioned above. The title of this paper refers to the minimum detectable energy only in

* Polaroid Corporation, Research Department, Cambridge, Massachusetts. Received 23 September, 1954.

order to indicate more clearly the general nature of the subject matter.

What is meant by the noise equivalent energy is easily understood in terms of the following simple experiment. Select a piece of photographic film. Let it be supposed that the characteristic curve (density versus logarithm of exposure) of the film is known for some given method of development. Pre-expose the film uniformly by some arbitrary amount, and develop the film by the given method. With a precise densitometer, measure the density of the film over a large number of circular regions of the film, all of the same area A. From the results compute the mean density $\bar{D}$, and also ΔD, the root-mean-square deviation of the density from the mean value $\bar{D}$. Then from the characteristic curve compute the increment of energy falling on the area A that will cause the density of the film to increase from $\bar{D}$ to $\bar{D} + \Delta D$. This energy increment is denoted by K_N and is called the *noise equivalent energy*. It is so called because it is the amount of energy that increases the density by an amount equal to the root-mean-square fluctuation of the density.

Evidently, the noise equivalent energy K_N has a numerical value that depends on

1. The area A.
2. The type of film selected.
3. The amount of the pre-exposure.
4. The spectral energy distribution of the radiation used in constructing the characteristic curve.
5. The method of development.

The dependence of K_N upon the first four of these items is examined in this paper.

The experimental observations by Dr. Albert Rose[9] of RCA suggest that for visual inspection of photographic film, the minimum detectable energy is about five times the noise equivalent energy. A similar determination by O. H. Schade[10] suggests that the ratio lies between three and six. This ratio can scarcely be expected to be a constant, since for visual inspection the detectability will depend also on the size and contrast of the test object.

No new *experimental* data are reported in this paper. The results reported here are based on data that have been published, or were supplied upon special request, by various members of the Eastman Kodak Company.

Part II. The Noise Equivalent Energy

The following definition is formulated in terms of the *density* fluctuation of the film. The primary reason for choosing the density rather than some other function of the transmittance, is that both the granularity data and the sensitometric data that will be used are expressed in terms of the density. A secondary reason is that density appears particularly appropriate for use in connection with a discussion of granularity.

In the following proposal of a definition of the noise equivalent energy, it is assumed that the film is exposed uniformly to a source of light, and that the film is then developed in a standard manner. Let this uniform exposure be called the *pre-exposure*.

The average density is then measured at each of a large number of randomly chosen circular regions of the film, each of the same area A. Let the density values of the regions be denoted by $D_1, D_2, \ldots, D_n$, where n is the number of regions whose density is measured. Be-

cause of the granularity of the image, these densities will not all be equal.

The average density $\bar{D}$ is defined by

$$\bar{D} = n^{-1} \Sigma_k D_k, \qquad k = 1, \ldots, n \qquad (2.1)$$

This is nearly equal to the density that would be measured with a densitometer of very large aperture. $\bar{D}$ will also be called the pre-exposure density. The root-mean-square fluctuation in density will be denoted by ΔD and is defined by

$$\Delta D = (n^{-1} \Sigma_k (D_k - \bar{D})^2)^{1/2} \, k = 1, \ldots, n \quad (2.2)$$

The noise equivalent energy K_N is now defined as that energy, incident uniformly upon the area A of the pre-exposed and undeveloped film, that causes the mean density of the developed film to increase from $\bar{D}$ to $\bar{D} + \Delta D$.

Both ΔD and K_N depend on the area A. The nature of this dependence is discussed in the next section.

The Selwyn Granularity Coefficient

Selwyn[11] has defined a coefficient of granularity S as follows

$$S = (2A)^{1/2} \Delta D \qquad (2.3)$$

where A is in square microns and where ΔD is, of course, a function of A. Selwyn's experimental results indicate that the granularity S is not quite independent of the area A of the scanning aperture, but tends to increase with A as the 0.05 to 0.10 power of A. This implies that ΔD varies inversely as the 0.40 to 0.45 power of A.

Jones and Higgins[1, 2] have studied the dependence of S upon the area A in considerable detail, and find that S has a maximum and then a minimum as the aperture diameter is increased from 5 microns to 320 microns for Super-XX film. The net result is that S is substantially independent of the area A for aperture diameters from 10 microns to 180 microns, but diverges from constancy somewhat more for larger or smaller apertures.

To the extent that the granularity S has been found to be independent of the area A, the dependence of ΔD upon the area is

$$\Delta D = \alpha A^{-1/2} \qquad (2.4)$$

where α is a constant that is independent of the area A, and that depends only on items 2, 3 and 5 of the list at the end of this part.

The Noise Equivalent Energy

Now consider the change in density produced by a signal that is incident upon an area A of a uniformly pre-exposed negative. Provided that the fractional variation of the slope of the characteristic curve is small over the range of signal exposures involved, the increase δD of the average density of the developed image will be proportional to the energy of the signal per unit area,

$$\delta D = \beta K / A \qquad (2.5)$$

where β is a constant that is independent of the area A, and that depends on items 2, 3, 4 and 5 of the list at the top of page 58. It should be noted, however, that the validity of the reciprocity law has been involved in the

statement of Eq. (2.5), insofar as the density increment is stated to be independent of the rate at which the energy K is supplied.

Suppose now that the energy K is supplied in a single pulse of duration τ. Then the power P of the pulse is related to K by

$$P = K/\tau \qquad (2.6)$$

From the last three equations, it follows that the power P_N required to produce a density increment δD equal to ΔD is given by

$$P_N = \frac{\alpha}{\beta} \frac{A^{1/2}}{\tau} \qquad (2.7)$$

and may be called the noise equivalent power. It follows immediately that the noise equivalent energy K_N is given by

$$K_N = \alpha A^{1/2}/\beta \qquad (2.8)$$

where α and β are both independent of both A and τ.

The Figure of Merit M_2

In a recent paper[12], it has been shown that many different types of radiation detectors may be placed in one of two mutually exclusive classes on the basis of the way that the noise equivalent energy depends on the speed of response. There are a number of subtleties connected with the general definition of the two classes, and the reader is referred to the paper cited for a full account. For the present purpose, however, the two classes may be defined as follows.

It is supposed that the construction of every detector considered is matched in optimum way to the area and duration of the signal to be detected. Then Class I detectors are those for which the following quantity is independent of the area A and the pulse duration τ.

$$K_N/(\tau A)^{1/2} = \text{independent of } A \text{ and } \tau. \qquad (2.9)$$

Similarly, Class II detectors are those for which the following quantity is independent of the area A and the pulse duration τ:

$$K_N/A^{1/2} = \text{independent of } A \text{ and } \tau. \qquad (2.10)$$

Evidently, the two classes are mutually exclusive.

By comparison of Eqs. (2.8) and (2.10), one concludes that the photographic negative is a Class II detector. In this connection, it should be emphasized that the area A is the area of the signal, not the area of the entire negative.

In another recent paper[13], figures of merit were defined for both Class I and Class II detectors. The figure of merit for Class II detectors is denoted by M_2 and is defined by

$$M_2 = 3 \times 10^{-15} A^{1/2}/K_N = 3 \times 10^{-15} \beta/\alpha \qquad (2.11)$$

where A is in square microns, and K_N is in joules.
The original definition[13] of M_2 indicates that M_2 is dimensionless, but in the form (2.11), dimensional constants have been absorbed in the numerical coefficient.

Bolometers and thermocouples are Class II detectors. The figures of merit M_2 for 50 different bolometers and thermocouples described in the literature are tabulated in reference 13. The best thermocouples[14] have figures of merit equal to about one.

To those who are familiar with photographic manipulations, it will be obvious that the noise equivalent energy of photographic materials will depend on the following items:

1. The signal area A.
2. The type of negative.
3. The amount of the pre-exposure.
4. The spectral energy distribution of the signal.
5. The method of development.

In Part V, where several photographic materials are discussed, the figure of merit will be maximized with respect to the wavelength of the signal and with respect to the pre-exposure. All of the results presuppose standard developing conditions.

Part III. A Fundamental Upper Limit on M_2

In the general theory of the performance of detectors[*] as described in reference 12, it is supposed that the only background against which signals are to be detected is the room temperature radiation field. The fluctuation in this field thus sets the fundamental upper limit on the detectivity.

In the special case of the photographic negative, however, one deliberately introduces an additional radiation background: that provided by the pre-exposure. The signal to be detected must be above the fluctuation in the pre-exposure.

The fluctuation in the pre-exposure can be calculated easily, and such calculation leads to a value of the figure of merit M_2 that cannot possibly be exceeded by any detector that operates in the presence of the given pre-exposure. This maximum possible value of M_2 will be denoted by $\mathbf{M_2}$.

The upper limit $\mathbf{M_2}$ that will be calculated is the figure of merit that would actually be obtained with a negative that was completely homogeneous (completely free of a grain structure), and in which the density of the given area A is exactly proportional to the number of photons absorbed in that area.

When a film is exposed uniformly, one should imagine the photons as striking the film in the same random manner that raindrops strike a horizontal surface. In such a random flow of discrete objects, it is well known that, upon repeated trials, the probability distribution is of the Poisson type—that is to say, the root-mean-square fluctuation Δn of the number striking a given area in a given time is equal to the square-root of the average number $\bar{n}$:

$$\Delta n = \bar{n}^{1/2} \qquad (3.1)$$

Actually, the expression just given is not precisely correct. It would be correct if the photons were completely random and thus obeyed Maxwell-Boltzmann statistics. Photons, however, obey Bose-Einstein statistics; accordingly, the expression should have the factor $(1 - e^{-h\nu/kT})^{-1/2}$ appended to the right hand side, if the radiation is in thermal equilibrium at the absolute temperature T[14]. This factor, however, is very close to unity for all ordinary light sources, and will be ignored henceforth.

Let K be the average energy incident on the area A during the pre-exposure of the film. The average number of quanta in the light is

$$\bar{n} = K/K_1 \qquad (3.2)$$

where K_1 is the energy of a single quantum:

$$K_1 = hc/\lambda \qquad (3.3)$$

The rms fluctuation ΔK in the energy incident upon the area A is thus

$$\Delta K = K_1 \Delta n \qquad (3.4)$$

or

$$\Delta K = (KK_1)^{1/2} \qquad (3.5)$$

The incident energy per unit area U is related to K by

$$U = K/A \qquad (3.6)$$

whence

$$\Delta K = (AUK_1)^{1/2} \qquad (3.7)$$

If the only cause of density fluctuation in the developed image were the fluctuation in the pre-exposure, the noise equivalent energy K_N would be equal to the rms fluctuation ΔK:

$$K_N = \Delta K \qquad (3.8)$$

From Eqs. (2.11), (3.7) and (3.8), one then concludes

$$\mathbf{M_2} = 3 \times 10^{-18}(UK_1)^{-1/2} \qquad (3.9)$$

where U is in joules/micron², and K_1 is in joules.

The derivation given so far has been oversimplified in that it has assumed that every photon incident on the negative contributes to the developed image. This is not the case. Only a fraction ϵ of the incident photons are absorbed in a photographically relevant manner[18]. The remaining photons are transmitted, reflected, or absorbed in a way that has no effect on the latent image.

We accordingly redefine the upper limit $\mathbf{M_2}$ as the figure of merit that would be obtained with a negative that was completely homogeneous and in which the density of the given area A is exactly proportional to the number of photons that are incident in that area, and that are absorbed in such a way that they are actually utilized in forming the latent image.

It is desirable, however, that the symbols n, K, and U continue to refer to the incident light. Accordingly, Eq. (3.1) must be rewritten

$$\Delta n = (\bar{n}/\epsilon)^{1/2} \qquad (3.10)$$

If now the derivation of (3.9) is repeated with (3.10) as the starting point, one finds

$$\mathbf{M_2} = 3 \times 10^{-18}(\epsilon/UK_1)^{1/2} \qquad (3.11)$$

where U is the incident power per unit area of the pre-exposure.

Unfortunately, the value of ϵ is not very well known. No published information is available that is known to hold for the specific films discussed in Part V.

Webb[18] has measured the value of ϵ for a non-color-sensitized single-grain-layer plate. In Webb's notation, ϵ is the product of two factors κ and α. The factor κ is the fraction of the incident light that is absorbed by the emulsion, and α is the fraction of the absorbed quanta that are actually utilized in forming the latent image. Webb's value of α is approximately $1/4$, for wavelengths in the range from 360 to 500 millimicrons. In a private conversation, Dr. J. H. Webb has suggested that the value $\kappa = 0.1$ is suitable for the grains of Super-XX film at 420 millimicrons.

These rough considerations suggest that the value of ϵ is roughly $1/40$ for panchromatic emulsions. This is confirmed by a letter dated January 29, 1947, from Dr. A. P. H. Trivelli of EK to Dr. Albert Rose of RCA, in which Dr. Trivelli suggests that the value of ϵ for sensitized emulsions like Super-XX and Tri-X is of the order 0.1. We therefore assume:

$$\epsilon = 0.025 \qquad (3.12)$$

We now anticipate the results to be found in Part V for the Super-XX film. It is found that the pre-exposure that maximizes the figure of merit M_2 is about 0.0025 meter-candle-seconds. By Eq. (5) of the Appendix, this corresponds to an incident power per unit area of

$$U = 5.0 \times 10^{-18} \text{ joule/micron}^2 \qquad (3.13)$$

when the radiation consists of blue light of wavelength 0.42 micron. For such light, the energy K_1 of a single quantum is

$$K_1 = 4.73 \times 10^{-19} \text{ joule} \qquad (3.14)$$

From the last four equations, one obtains the following upper limit on the figure of merit M_2

$$\mathbf{M_2} = 310 \qquad (3.15)$$

for Super-XX film. It is reassuring that this upper limit is greater than the experimental value 220 found in Part V.

The fact that M_2 and $\mathbf{M_2}$ are not too far apart, however, does suggest that *an appreciable part of the actual granularity of Super-XX film is due to the quantum fluctuation of the light that constitutes the exposure*. This suggestion is believed to be novel.

The data used to evaluate ϵ are quite rough, and therefore little confidence can be placed in the result found above that $\mathbf{M_2}$ is not much greater than M_2. If, however, this result should be confirmed by more reliable data, then a major part of the observed granularity of Super-XX film would be due to quantum fluctuation of the light that forms the latent image. If this were so, furthermore, one would at last have an explanation for the "clumping" phenomenon that has long perplexed photographers.

It is well known that the granularity of sensitive films is substantially greater than the amount that would be obtained if the developed grains were randomly distributed; the grains appear to "clump". Furthermore, every dark-room operator knows that more energetic development of an underexposed negative increases the granularity of the developed image over that of a more fully exposed negative. Both of these facts are just what one would expect if the major part of the granularity is due to the fluctuations in the light that forms the latent image. In this case, the granularity is part

of the image, and any process that helps to bring out a weak image will also bring out the weak image due to the quantum fluctuations.

The suggestions made in the above two paragraphs must be regarded as speculative, because of the inconclusive nature of the experimental data. It is hoped, however, that these speculations will motivate someone to make a quantitative examination of the proposal.

Part IV.
Transformation of the Expression for M_2

It is regretted that the available data on photographic materials are not in a form that permits direct calculation of the numerical value of the figure of merit M_2 for widely known films. It is unfortunately necessary, therefore, to have recourse to a number of different sources of information, and in many cases to use data for purposes for which they were not intended.

In this Part, the expression given above for the figure of merit M_2 will be transformed so that it is expressed in parameters that are of more direct photographic significance. This will permit the immediate use of available photographic data.

As above, let K be the energy in joules incident on area A, let U be the energy per unit area in joules per square micron, and let E be the exposure in lumens per square meter (meter-candle-seconds). Let Δ be used temporarily to indicate a small increment of a quantity.

Then one has

$$\Delta K = A \Delta U \qquad (4.1)$$

or

$$\Delta K = A \frac{dU}{dE} \frac{dE}{dD} \Delta D = A \frac{U}{E} \frac{dE}{dD} \Delta D \qquad (4.2)$$

If now ΔD be interpreted as the rms fluctuation of the density D, then ΔK becomes the noise equivalent energy:

$$K_N = A \frac{U}{E} \frac{dE}{dD} \Delta D \qquad (4.3)$$

The last relation is, of course, valid only if the relation between the energy K and the density D is reasonably linear for densities in the range $\bar{D} - \Delta D$ to $\bar{D} + \Delta D$. In the following, we assume that this condition holds.

The expression (2.11) for the figure of merit M_2 now becomes

$$M_2 = 2^{1/2} \times 3 \times 10^{-13} \frac{E}{U} \frac{1}{S} \frac{dD}{dE} \qquad (4.4)$$

where the relation (2.3) has also been employed.

The ratio E/U, the derivative dD/dE, and also the figure of merit M_2, evidently depend upon the spectrum of the radiation. The data to be used in Part V are obtained with ASA sunlight. If these data were used directly, the figure of merit would be for sunlight. In a fundamental investigation of this kind, however, it seems more appropriate to obtain the figure of merit for monochromatic radiation.

Accordingly, the expression (4.4) will be rewritten in the following form:

$$M_{2\lambda} = 2^{1/2} \times 3 \times 10^{-13} \frac{E_s}{U_\lambda} \frac{1}{S} \frac{dD}{dE_s} \qquad (4.5)$$

where $M_{2\lambda}$ is the figure of merit for monochromatic radiation of wavelength λ. U_λ is the energy incident per unit area, it being assumed that the energy consists of monochromatic radiation of wavelength λ; U_λ is expressed in terms of joules per square micron. E_s is the exposure to sunlight of the quality specified by the American Standards Association, it being assumed that the exposure is chosen so that its effectiveness is the same as that represented by U_λ; E_s is expressed in terms of lumen-seconds per square meter.

The ratio E_s/U_λ has approximately the same value for all panchromatic emulsions, and is found in the Appendix to have the approximate value

$$\frac{E_s}{U_m} = 4.68 \times 10^{14} \text{ lumens/watt} \qquad (4.6)$$

for panchromatic films, and wavelength $\lambda_m = 0.42$ micron. The value of the ratio for other wavelengths may be obtained by multiplication by the function $W(\lambda)$ plotted in Figure seven of the Appendix.

From the last two equations one obtains the following expression for the figure of merit M_2 for panchromatic emulsions and for monochromatic radiation of wavelength 0.42 micron.

$$M_{2m} = 1.99 \frac{1}{S} \frac{dD}{dE_s} \qquad (4.7)$$

This expression for the figure of merit may be evaluated if one knows (a) the Selwyn granularity as a function of density, and (b) the density as a function of exposure to sunlight. Both of these relations are determined for four different types of panchromatic film in Part V.

Table II

GRANULARITY DATA FOR THE FOUR FILMS

	D_0	S_0 microns	M_{2mm}/S mcs
Tri-X	0.42	2.00	1.17
Super-XX	0.19	0.90	1.89
Pan-X	0.40	0.775	2.96
FG Neg.	0.07	0.20	5.69

Part V.   Results on Four Specific Films

In this Part, the figure of merit will be obtained for four different Kodak negative films as a function of the pre-exposure and as a function of the wavelength of the radiation.

Unfortunately, it was not possible to obtain a complete set of data for any one emulsion number. The information needed was obtained from a variety of sources. This means that the accuracy of the final results is not as high as it would be if all of the data were obtained on nearly identical film. Presumably, the results apply only to the average run of the manufactured film and then with fair accuracy only.

It is therefore to be hoped that the present paper will encourage others to obtain results of greater accuracy, and for a greater variety of film types.

The four films for which quantitative results will be obtained are shown in Table I. The full name of the film is shown in the first column, and the abbreviation used in the paper is shown in the second column. The third and fourth columns give the name of the developer and the duration of the development in a sensitometric developing machine[17] with the solutions held at a temperature of 20 C. These four columns are copied from reference 2.

Sources of Information

The granularity data for the four films were obtained from reference 2. Sensitometric curves for the four materials for exposure to sunlight were kindly supplied by Mr. J. W. Goda,[18] Government Sales Division, Eastman Kodak Company.

It is not obvious that the developing conditions specified in Table I will yield the same gamma for films manufactured in different years. Accordingly, an effort was made to determine the effective gamma for the developed films from several sources of information. The values of γ_1 in the first column of Table I are from reference 1. (Materials 2, 5, and 8 assumed to be similar to materials I, III, and IV of reference 2.) A private communication from Dr. Higgins[19] indicates that the successive density values in Table III and IV of reference 2 correspond to exposure increments by a factor of $2^{1/5}$; values of gamma obtained by this means from reference 2 are denoted in the table by γ_2. Values of gamma for materials I and II are given in the Kodak publication dated June, 1946, "Kodak Materials for Aerial Photography." From this publication, which is contemporaneous with reference 2, were obtained the values of gamma denoted by γ_3 listed in Table I. Finally, the values of gamma indicated on the plots supplied by Mr. Goda are given in the last column of Table I and are denoted by γ_4.

Table III

DEPENDENCE OF THE SELWYN GRANULARITY S ON THE DIAMETER ϕ OF THE SCANNING APERTURE FOR TRI-X FILM AT A DENSITY OF 0.42 (FROM TABLE V OF REFERENCE 2).

ϕ microns	S microns
5.3	2.09
10.7	1.89
20.2	2.03
39.9	2.00

In summary, the gamma to which the film was developed is given by γ_1, γ_2 or γ_3 for the granularity data used here, and is given definitely by γ_4 for the sensitometric data used in this paper.

The only marked discrepancy to be noted in Table I is for the Super-XX negative. The 1951 value of gamma (1.82) is substantially above the 1946–47 values (about 1.3.). Presumably, this represents a difference in the film manufactured at these different dates.

Relation between S and D

It is desirable to have an approximate mathematical expression for the relation between the Selwyn granularity S and the density D. Such an expression not only serves to smooth the scatter in the granularity data, but also facilitates the evaluation of M_2 for a number of different pre-exposures.

If the grains were distributed randomly in the emulsion, one would expect that the Selwyn granularity would be proportional to the square root of the density. The data given by Jones and Higgins in reference 2 are nearly, but not exactly, in accord with this expectation. The granularity versus density data tabulated in Tables III and IV of reference 2 for the FG Neg. and Super-XX films are re-plotted with logarithmic scales in Figures one and two of the present paper. For each of the seven sets of data shown in these figures, a straight line that best fits the point has been drawn. The slope of each of these seven lines is indicated in the figures. The best fitting straight lines have a slope that is consistently less than the one-half suggested by theory, and is approximately 0.4 for the lines whose slope is determined most reliably. The slope is perhaps slightly less than 0.4 for the FG Neg. and perhaps slightly greater than 0.4 for Super-XX.

The 0.4 power law indicated by Figures one and two may be written

$$\frac{S}{S_0} = \left(\frac{D}{D_0}\right)^{0.4} \tag{5.1}$$

where S_0 is the granularity at the arbitrarily chosen density D_0. Upon eliminating S between (4.7) and (5.1), one obtains

$$M_{2m} = 3.31 \ (D_0^{0.4}/S_0)\mathcal{S} \tag{5.2}$$

where

$$\mathcal{S} = dD^{0.6}/dE, \tag{5.3}$$

The derivative $\mathcal{S}$ may be obtained directly from the D versus log E, curve of the photographic material in question.
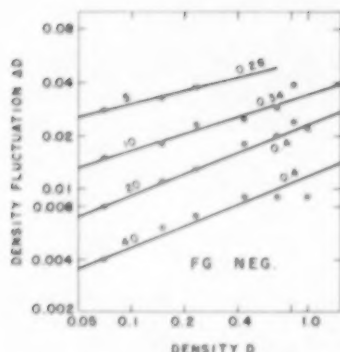
Fig. 1. The root-mean-square density fluctuation ΔD plotted as a function of the density D, for Super-XX film. The coordinate scales are logarithmic. The points represent the measurements of Jones and Higgins. The lines are drawn as the best fit to the experimental points. All of the lines are drawn with a slope of 0.40. The labels on each line at the left is the diameter of the scanning aperture in microns.

Determination of D_0 and S_0 for the Four Materials

Table II shows values of S_0 and D_0 for each of the films. The values for three of the films are obtained from Tables III, IV, and V, which show the dependence of the Selwyn granularity S on the diameter ϕ of the scanning aperture. The data in Tables III, IV, and V were obtained from reference 2. The values for Pan-X film were found by the more complex process of first establishing an empirical relation between Goetz-Gould granularity and Selwyn granularity, and then using this relation to interpret the data on the Goetz-Gould granularity of Pan-X film given in reference 2.

Upon substituting these values of S_0 and D_0 in Eq. (5.2), one finds the M_{2mm}/S ratios shown in the last column of Table II.

Sensitometric Data

The granularity data having been summarized, it remains to examine the sensitometric data available for the four films.

From the plot of D versus log E_s, supplied by Mr. J. W. Goda, the information plotted in Figure three for Tri-X film was obtained. In this figure, the middle curve shows the relation between D and E. The logarithmic scale chosen for the ordinate emphasizes the toe of the curve, which toe is the part of greatest interest in the present connection. The bottom curve shows the derivative $dD^{0.4}/dE_s$, abbreviated by the symbol S. It will be noted that this curve passes through a maximum at a value of log E_s equal to -2.85. Clearly, this pre-exposure is that which yields a minimum noise equivalent energy, and the maximum figure of merit. Finally, the top curve shows the gradient g of the characteristic curve, defined as the derivative $dD/d \log E_s$.

Similarly, Figures four through six show corresponding data for the other three films.

The density D employed in this section is the density of the film above the base density; it is not the density above the fog, because the fog itself introduces granu-

Table IV

DEPENDENCE OF THE SELWYN GRANULARITY S ON THE DIAMETER ϕ OF THE SCANNING APERTURE FOR SUPER-XX FILM AT A DENSITY OF 0.42 (FROM TABLE III OF REF. 2).

ϕ microns	S microns
5.3	0.73
10.7	0.98
20.2	1.04
39.2	0.85
79.8	0.80
156.9	0.98

larity. The base densities for the four materials are 0.05, 0.04, 0.25, and 0.20, respectively.

Table V shows the values of some of the parameters for the pre-exposure that maximizes S.

Substitution of the values of S_{max} in Table VI into the values of M_{2mm}/S in Table II yields the values of the figure of merit M_{2mm}, defined as the figure of merit M_2 for 0.42 micron blue light at the optimum pre-exposure. These values are shown in Table VI. The figure of merit for other wave-lengths may be obtained by multiplication by the function $W(\lambda)$ plotted in Figure seven of the Appendix. Similarly, the figure of merit for other pre-exposures may be obtained upon multiplication by S/S_{max}. These statements may be summarized by the following equation:

$$M_{2\lambda} = M_{2mm}W(\lambda)S/S_{max} \qquad (5.4)$$

According to Table VI, the figure of merit M_2 of Super-XX and Tri-X films is approximately 200, and is therefore about 200 times the figure of merit of the best thermocouples, since these have a figure of merit of about unity.

It must be recognized that the figure of merit M_2 measures only one of the many considerations that are of importance in the practical use of detectors. A thermo-
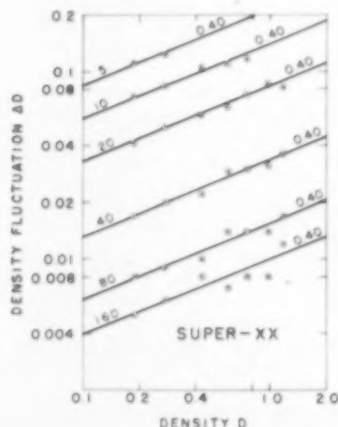

Fig. 2. Data corresponding to that in Fig. 1, for FG Neg. film. The slope of each of the lines is indicated at the right, and the diameter of the scanning aperture in microns is indicated on the left. For the two smallest apertures, the slope is less than 0.40.

Table V

ϕ microns	s microns
5.3	0.19
10.7	0.20
20.2	0.20
39.9	0.20

Table VI

VALUES OF SEVERAL QUANTITIES AT THE EXPOSURE THAT MAXIMIZES s

	$-\log E$	S_{max} (mcs)$^{-1}$	D_m	g_m	g_m/γ_4
Tri-X	2.85	144	0.165	0.40	0.328
Super-XX	2.58	118	0.202	0.63	0.346
Pan-X	2.12	25.5	0.137	0.33	0.300
FG Neg	0.72	0.72	0.073	0.193	0.280

couple with a time constant of 10 milliseconds may be used to make repeated measurements 100 times a second, or about 10 million times a day, whereas a film may be used only once. On the other hand, one large sheet of film may take the place of 10 million thermocouples for simultaneous measurements. Thermocouples are limited to the range of time constants from about one millisecond to about one second, whereas the range of exposure durations that obey the reciprocity law is much larger for some films. The photographic process is limited in the long wavelength direction at about 1.2 microns, whereas thermocouples are sensitive to far infrared radiation and radio waves.

If, however, one is willing to employ conditions of measurement that are appropriate for both films and thermocouples—signal durations from 0.01 to 0.1 second, detector area about one square millimeter, signal wavelength around 0.4 micron—then one may say with confidence that Super-XX film will be able to detect an amount of energy roughly 200 times smaller than the minimum detectable energy of a thermocouple.

Empirical Criterion for the Optimum Pre-exposure

The optimum pre-exposure has been defined as the pre-exposure that maximizes the derivative s defined by Eq. (5.3). This derivative may be computed for any given D versus $\log E$ curve. The computation is somewhat tedi-
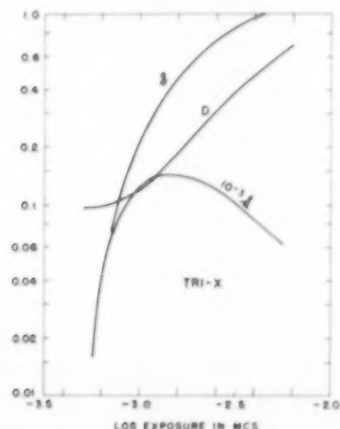
ous, however, and it is therefore of interest to inquire whether a more simple criterion is available.

For the four materials studied in this Part, such a simple criterion is available. Table V shows in the fifth column the gradient g_m of the D versus $\log E$ curve at the exposure that maximizes s, and shows in the sixth column the ratio of the gradient g_m to the maximum gradient γ_4 that is tabulated in Table I. All of the four values of this ratio in Table V lie within 10 per cent of the average value 0.313.

Thus, insofar as these four specific examples can determine a general rule, they indicate that the pre-exposure that yields the minimum value of the noise equivalent energy is equal to the pre-exposure for which the gradient g of the characteristic curve is equal to 0.3 times the maximum gradient γ.

$$g = 0.3\gamma \qquad (5.5)$$

Illustrative Values of the Noise Equivalent Energy K_N

No numerical values of the noise equivalent energy K_N have been given so far in this report. The reason, of course, is that K_N depends upon the area A, whereas the figure of merit M_2 is invariant in this respect.

In order to give a value of K_N, one must first select an area A. Since K_N decreases in proportion to the square root of A, it is of interest to inquire how small the area may be.

Fig. 3. The density D, the gradient $g = dD/d \log E_o$, and the derivative $s = dD^{2}/dE$, plotted as functions of the exposure E, in meter-candle-seconds of sunlight, for Tri-X film. The coordinate scales are logarithmic.
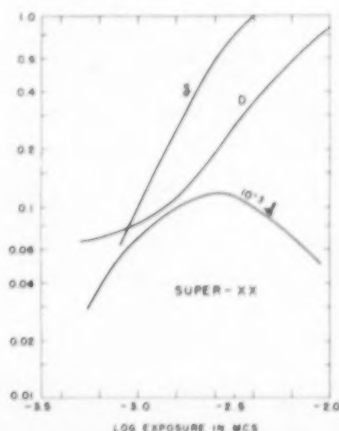

Fig. 4. The density D, the gradient g, and the derivative s, plotted as functions of the exposure E, in meter-candle-seconds of sunlight, for Super-XX film. The coordinate scales are logarithmic.

Table VII

Material	M_{2mn}
Tri-X	170
Super-XX	220
Pan-X	75
FG Neg.	4

Evidently, it would make no sense to choose an area A so small that the density fluctuation computed from (2.3) is larger than the density itself. One computes easily from the values of S_0 and D_0 given for Super-XX in Part V that the rms density fluctuation will be 0.05 at a density of 0.2 for an area A equal to 160 square microns. This corresponds to a circular area 15 microns in diameter. Since for this area the density fluctuation is only $1/4$ of the density, it is reasonable to suppose that the figure of merit M_2 may be used to compute the value of K_N for this area.

For a material with a figure of merit M_2 equal to 200, the noise equivalent energy K_N for an area A equal to 160 micron^2 is by Eq. (2.11)

$$K_N = 1.9 \times 10^{-9} \text{ erg} \tag{5.6}$$

This energy corresponds to 400 photons of 0.42 micron radiation, and is equal to 1200 electron-volts. The minimum detectable energy, being about five times K_N, is about 10^{-8} erg.

It should be noted that these energies are those of the *incident* radiation. The effectively absorbed energy is probably about 0.025 K_N, or about 50 photons.
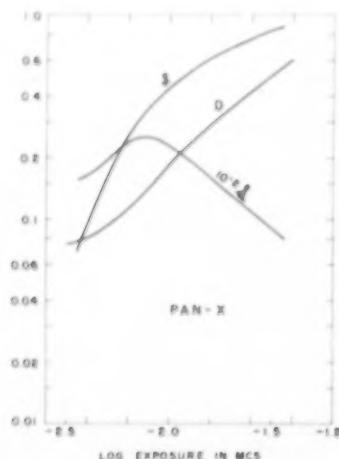
Acknowledgment

Fig. 6. The density D, the gradient g, and the derivative δ, plotted as functions of the exposure E_0 in meter-candle-seconds of sunlight, for FG Neg. film.

Appendix

In this appendix, the ratio E_s/U_λ will be computed as a function of λ for panchromatic negative films. The quantities E_s and U_λ are defined above in the text following Eq. (4.5).

Let $W(\lambda)$ be the spectral energy distribution of sunlight, normalized to one joule per unit area per millimicron wavelength range at the maximum of the distribution. This will be called "normalized sunshine." Let $L(\lambda)$ be the relative sensitivity of the human eye for cone vision as a function of the wavelength λ, normalized to a maximum value of unity. Let $P(\lambda)$ be the relative sensitivity of the photographic material, as a function of the wavelength, normalized to a maximum value of unity; the wavelength of the maximum is denoted by λ_m.

Then $650 L(\lambda)W(\lambda)$ is the spectral distribution of the luminance of normalized sunlight, expressed in lumen-seconds per unit area per millimicron of wavelength range. The number 650 is the number of lumens per watt for monochromatic radiation of wavelength 0.555 micron. $P(\lambda)W(\lambda)$ is the spectral distribution of the photographically effective energy in ASA sunshine.

Then $\mathcal{L}$ defined by

$$\mathcal{L} = 650 \int_0^\infty L(\lambda)W(\lambda)d\lambda \tag{1}$$

is the lumen-seconds per unit area of normalized sunshine, and $\mathcal{U}$ defined by

Fig. 5. The density D, the gradient g, and the derivative δ, plotted as functions of the exposure E_0 in meter-candle-seconds of sunlight, for Pan-X film. The co-ordinate scales are logarithmic.
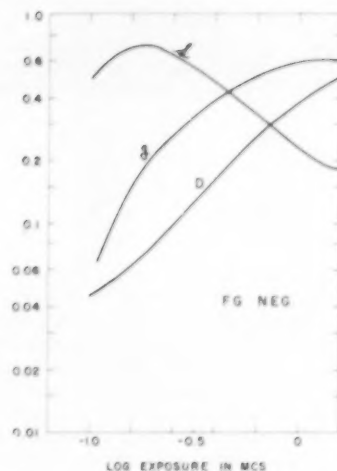
$$\mathcal{U} = \int_{L}^{\infty} L(\lambda)W(\lambda)d\lambda \qquad (2)$$

is the number of joules per unit area of monochromatic radiation of wavelength λ_m that produces the same photographic effect as normalized sunshine.

The ratio $\mathcal{L}/\mathcal{U}$ would be identical with the ratio E_s/U_m except for the fact that E_s is referred to a square meter, whereas U_m is referred to a square micron. One therefore has

$$E_s/U_m = 10^{12}\mathcal{L}/\mathcal{U}$$
$$= 650 \times 10^{12} \frac{\int L(\lambda)W(\lambda)d\lambda}{\int P(\lambda)W(\lambda)d\lambda} \qquad (3)$$

Evidently, this expression is independent of the normalization of $W(\lambda)$. Henceforth, $W(\lambda)$ will be normalized with unity as its maximum value. Thus all three of the functions $W(\lambda)$, $L(\lambda)$ and $P(\lambda)$ are so normalized.

Figure seven shows the spectrum $W(\lambda)$ of sunshine, as obtained with a 2700 K source corrected to mean noon sunlight with the Davis-Gibson filter shown in Chart 6 of reference 20. Figure seven shows also the normalized ICI tristimulus value $\bar{y}$, obtained from Table XII of reference 21 and here denoted by $L(\lambda)$. Finally, Figure seven shows the normalized sensitivity $P(\lambda)$ of panchromatic emulsions, obtained from the curve for Panatomic-X film shown in Figure twelve of reference 22.

From the data in this figure, the products $L(\lambda)W(\lambda)$ and $P(\lambda)W(\lambda)$ were computed, and are plotted in Figure eight. By numerical integration, one finds that the areas under the two curves are
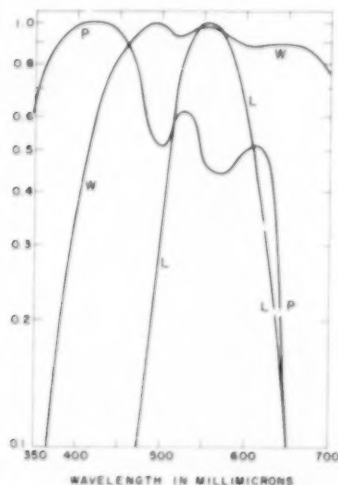

Fig. 7. The spectrum $W(\lambda)$ of sunlight, the relative sensitivity $P(\lambda)$ of panchromatic negatives, and the relative sensitivity $L(\lambda)$ of the human eye, all normalized to a maximum value of unity, plotted as a function of the wavelength λ in millimicrons. The ordinate scale is logarithmic, and the wavelength scale is linear.
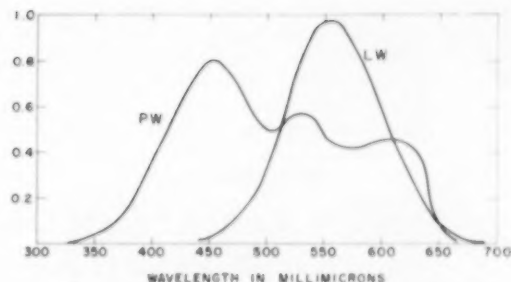

Fig. 8. The products $P(\lambda)W(\lambda)$ and $L(\lambda)W(\lambda)$ plotted as a function of the wavelength λ in millimicrons. The coordinate scales are linear. The areas under the two curves have the ratio 0.72.

$$\int L(\lambda)W(\lambda) = 99.8 \text{ millimicrons} \qquad (4)$$
$$\int P(\lambda)W(\lambda) = 138.8 \text{ millimicrons}$$

Equations (3) and (4) now yield

$$E_s/U_m = 4.68 \times 10^{14} \text{ lumens/watt} \qquad (5)$$

which is the result given in Eq. (4.6). The ratio E_s/U_λ is obtained from Eq. (5) upon multiplication by $P(\lambda)$:

$$E_s/U_\lambda = (4.68 \times 10^{14} \text{ lumens/watt}) P(\lambda) \qquad (6)$$

References

1. L. A. Jones and G. C. Higgins, J. Opt. Soc. Am., Vol. 35, pp. 435-457 (1945).
2. L. A. Jones and G. C. Higgins, J. Opt. Soc. Am., Vol. 36, pp. 203-227 (1946).
3. L. A. Jones and G. C. Higgins, J. Opt. Soc. Am., Vol. 37, pp. 217-263 (1947).
4. L. A. Jones and G. C. Higgins, J. Opt. Soc. Am., Vol. 38, pp. 398-405 (1948).
5. L. A. Jones and G. C. Higgins, J. Opt. Soc. Am., Vol. 41, pp. 41-52 (1951).
6. L. A. Jones and G. C. Higgins, J. Opt. Soc. Am., Vol. 41, pp. 64-75 (1951).
7. L. A. Jones and G. C. Higgins, J. Opt. Soc. Am., Vol. 41, pp. 192-200 (1951).
8. L. A. Jones, G. C. Higgins and K. Stultz, J. Opt. Soc. Am., Vol. 45, p. 107-112 (1955).
9. Albert Rose, J. Opt. Soc. Am., Vol. 38, pp. 196-208 (1948).
10. O. H. Schade, RCA Review, Vol. 9, pp. 5-37 (1948).
11. E. W. Selwyn, Phot. J., Vol. 79, pp. 513-524 (1939).
12. R. Clark Jones, J. Opt. Soc. Am., Vol. 39, pp. 327-343 (1949).
13. R. Clark Jones, J. Opt. Soc. Am., Vol. 39, pp. 344-356 (1949).
14. R. Clark Jones, Advances in Electronics, Vol. 5, pp. 1-96 (1953) pp. 20-22.
15. Ludwik Silberstein and A. P. H. Trivelli, J. Opt. Soc. Am., Vol. 35, pp. 93-107 (1945).
16. J. H. Webb, J. Opt. Soc. Am., Vol. 38, pp. 312-23 (1948).
17. L. A. Jones, M. E. Russell and H. R. Beacham, J. Soc. Mot. Pict. Eng., Vol. 28, pp. 73-98 (1937).
18. Private communications dated January 30, 1951, and February 20, 1951.
19. Private communication dated February 6, 1951.
20. Raymond Davis and K. S. Gibson. Filters for the reproduction of sunlight and daylight and the determination of color temperature. Miscellaneous Publication, Bureau of Standards, No. 114, 1931.
21. Arthur C. Hardy, Handbook of Colorimetry (Technology Press, 1936).
22. Photographic plates for scientific and technical use (Eastman Kodak Company, 1948), sixth edition.

COLOR CORRECTION APPLIED IN THE SIGNAL CORPS PHOTOGRAPHIC LABORATORY

Louis Werner*

ABSTRACT

Color transparencies are sent in from all parts of the world to the Signal Corps Color Laboratory. The transparencies often of greatest military value have been exposed and processed under extremely unfavorable conditions. This paper deals with methods used to rectify color deviations.

IN MOST commercial color photographic establishments color control starts when the color film is exposed and processed. Reproduction is not undertaken until a technically satisfactory transparency has been achieved. The U. S. Army Signal Corps, like many commercial finishing laboratories, has a special problem. Transparencies are received from all parts of the world and many of them, indeed often those of greatest military value, have been exposed and processed under extremely unfavorable conditions such as those resulting from combat and severe climatic factors.

The Signal Corps uses every artifice it knows to rectify color deviations. Though the methods are not all unique or new, an effort has been made to arrange and classify them so that technical considerations or expediency will govern their application according to circumstances.

Two general classifications distinguish the manual color correction techniques applied by the artist from the chemical and physical color correction techniques applied by the photographer. While it is true that the artist must be well informed about color photography if he is to apply his various mediums usefully, he is not as much concerned with emulsion characteristics, theories of development and the like as he is with color theory, colorants, and techniques associated with painting. Manual color corrections are applied locally to selected areas of the subject. Physical or chemical color corrections are applied to the whole subject according to known principles of the photographic processes. The stage of the reproduction process at which art work or manual correction is applied is largely determined by expediency. Chemical or physical corrections are applied at those stages of the reproduction process that technically permit.

It is rarely necessary or even desirable to reproduce exactly the psychophysical luminances and chromaticities of the scene or object photographed. Photographers, able to analyze a visual situation clearly, will actually *distort* the colors and brightnesses of a scene or object to compensate for determinants of final perception that would otherwise be lacking in the reproduction.

The term "color correction", as used in this paper, therefore, refers to changes necessary to bring about a more *convincing* representation of the scene or object photographed; that is to say, to make the photograph *appear* as much like the scene or object as possible.

In a particular photograph inadequate distribution of light has resulted in over exposure of important areas. Since the deficiency of detail and color cannot be repaired photographically, recourse must be had to manual application directly to the original transparency. Imbibition dyes as well as the water-soluble dyes used by colorists of black-and-white prints are suitable and should be applied with a sable brush of appropriate size to the back of the film rather than to the emulsion side.

The success of the operation is dependent on the skill of the artist and the degree of correction necessary, but the results in most cases, are more photographic in effect than those attained by the application of dyes or pigments to a color print.

In some cases deficiencies exist in localized areas of the subject when, for example, shadow portions have received insufficient illumination in areas of low luminance. Dye applied manually to the mask or applied to the separation negative can effect complete correction or at least an improvement. Incidentally, this technique may be combined with negative retouching to restore a semblance of detail as well as color to the shadow.

In portraiture, the desirability of negative retouching and facial make-up is still, and probably always will be, a controversial subject. These physiognomic artifices are, however, widely practised and cannot be ignored. Negative retouching in color on separation negatives requires all the skill and artistry of black-and-white portrait retouching plus a thorough knowledge of subtractive color synthesis. Not only must identical areas in three negatives be retouched, but also the amount of lead or medium applied must be apportioned to each negative according to the color correction desired.

Negative retouching, of course, is an implement of color correction for other subjects besides portraits. Its application also to the removal of minor color blemishes in color photographs is a generally accepted procedure.

Manual color correction can be applied at various stages of the reproduction process. Even the matrices prepared for a dye transfer print can be hand colored in the manner of the Flexichrome process.

Since color correction filters may be employed successfully when exposing color film, it might seem plausible to put them to the same uses when making separation negatives. Study of the principles involved discloses at once the inadvisability of such a procedure. The spectral sensitivities of each of the three layers of a color film differ from one another; whereas in separation the spectral sensitivity of the three films is uniform and only the energy distribution of the light source is altered by the separation filters. Furthermore, the subtractive action of two or more color filters applied in succession is unpredictable in terms of the visual appearance of the colored objects involved, so there would be little control over the selection of correction filters.

Separation negatives or masks may, however, be altered with respect to their gamma to correct erroneous color in shadow or highlight portions of the transparency. For example, by altering exposure and development of the green-filter negative a favorable adjustment can be made in the shadows of a picture without undue hue shift in the rest of the scale.

The effectiveness of masks in color correction is well understood. Though normally employed in a prescribed manner to compensate for inherent deficiencies of dyes or pigments used in the reproduction process, masks are also a helpful implement when compensating for deficiencies in the original transparency to be reproduced. Filters of great variety are available and may be used when exposing the mask to bring about desired change or correction in the reproduction of a color transparency. Foreknowledge of the relative energy of the filtered illuminant, and relative sensitivity of the masking film will enable a prediction to be made of the spectral regions which will be affected by the mask.

Color correction filters are introduced at any convenient point of the optical system when duplicating color transparencies. A primary correction is made to compensate for the response of a particular emulsion under prevailing standard conditions of illumination and color film processing. A secondary correction is then applied to compensate for undesirable color characteristics which are apparent in the transparency to be reproduced. Since there is no selective action with respect to the areas or densities affected, filter corrections of this kind are especially applicable to transparencies which exhibit an overcast of one color or another. The selection of filters for correction is largely accomplished by visual inspection; though there is little latitude for error, skill and experience combine to overcome the difficulty.

It has been generally known for a considerable time that the layers of an Ektachrome film can be selectively bleached.* The object of recent investigations was to determine to what extent the chemical action is confined to a single layer and also what control can be exercised over the operation. To this end a series of neutral scales on Ektachrome film were subjected to identical treatment for variable intervals of time to affect the cyan layer. The bleaching action is substantially confined to the cyan layer; densitometric measurements disclose a slight loss of saturation in the magenta and yellow layers. During the time interval of 2 minutes to 10 minutes the chemical action proceeds at a uniform rate thus affording excellent control.

A similar test was performed with a bleach intended to remove color from the yellow layer. Again it was found that the action is, for practical purposes, confined to the single layer and that the chemical action on a fixed concentration/variable time basis was controllably progressive. In all these tests temperature was maintained at a 70 F constant.

To determine an effective and convenient strength of bleach, a constant time/variable concentration series of tests were run. In such cases the chemical action shows uniform progression, but, since small quantities of some chemicals are required in the compounding of the solutions and since the solutions are not stable for any considerable length of time, it was considered more expedient to control the bleaching by variations in time.

Color corrections may be applied to the matrix in procedures involving dye-transfer reproduction. It has been found that strongly caustic solutions, for example sodium hydroxide, can be diluted to the point where they may be applied to a matrix without immediate dissolution of the whole gelatin image. The highlight portions are attacked first, so, taking great precaution not to carry the action too far, it is possible to improve prints involving line-work by cleaning out or *etching* any residual background tone.

The corrections that can be accomplished by adding acid, buffer and highlight reducer to the first matrix rinse constitute such standard operating procedure that mention of it is made here only for the sake of completeness.

The *manual* corrections described are, in reality, only a limited number of methods and combinations of methods that can be introduced at various stages of the reproduction process. In fact, the main limitations are those imposed by the skill and ingenuity of the artist and the photographer.

The chemical and physical corrections, however, are circumscribed by scientific principles in both their application and control. It is hoped this paper, which is primarily a résumé of the subject, will stimulate sufficient renewed interest in color correction procedures to move a reader to further investigation of some particular phase. Any one of the corrections described is a fitting subject for research and development.

Acknowledgment is made to the laboratory staff and to the Commanding Officer of the Signal Corps Photographic Library and Laboratory and to his staff of officers for their help and encouragement and for the opportunity afforded to participate in an activity so important to the progress of photography as the PSA Convention.

DESENSITIZATION AND THE STRUCTURE OF DESENSITIZING AGENTS

Lester Horwitz and Joseph S. Friedman[*]

ABSTRACT

Inspection of the many compounds which function as densitizers in the photographic process shows that a common relationship exists, which may clarify the desensitizing action displayed by these seemingly diverse structures. These agents appear capable of forming associations with an electron in the presence of a silver ion. A free radical capable of resonance stabilization results from this association, with a concomitant loss of an electron to the photographic process.

In view of the variety of organic structures which cause desensitization in the photographic emulsion one searches for some common relationship which will correlate the desensitizing action. Many of these desensitizing compounds are dyes. Among the interpretations advanced for desensitization are: (1) *Filter Action*. Here the desensitizer acts by screening out the irradiating light. This explanation was advanced quite early by Eder.[1] More recently Spence and Carroll[2] have shown that filter action alone cannot account for the desensitization exhibited by the dyes they tested. (2) *Replacement*. In this view, the desensitizer simply displaces the sensitizing dye at some sensitivity spot. Desensitization in such a case would be expected to have effect on the optically sensitized ranges of photographic response only. (3) *Oxidizing Power of the Desensitizer*. Desensitization in this circumstance is visualized as the ability of the desensitizer to abstract an electron from the latent image silver. This effect can occur under activation by light,[3] or without such activation.[4] Further, the desensitizer may act as a sensitizer or catalyst for the oxidation of the latent image silver by another substance, say light or atmospheric oxygen.[5] The use of dyes to sensitize oxygen oxidation of organic substances to visible light has been excellently reported by Schenck and coworkers.[6] The desensitizer may catalyze the oxidation or destruction of the sensitizing dye.[7] (4) *Association*. In this instance, the desensitizer does not displace the sensitizing dye but associates with it and renders sensitization ineffective.[8] Only induced sensitivities should be affected.

The interpretations listed above[9] do not account for the desensitizing powers exhibited by sensitizing dyes themselves. It is well established that such powers exist, often limiting the usefulness of the dye, and that desensitization by a sensitizing dye is an independent function, unrelated to its sensitizing capabilities.[2] The sensitizing capabilities of desensitizing dyes is a subject of considerable interest and must also be explained. Finally, it is well known that the replacement of a —CH— by a —N— in the methine chain connecting two heterocyclic moieties of a sensitizing dye can convert a good sensitizer to a powerful desensitizer. This is true if in the resulting structure the nitrogens of the chromomorphic chain are separated by an even number of carbon atoms. However, if the structure resulting from such replacement contains a chromophoric group with the nitrogens separated by an odd number of carbon atoms the sensitizing properties are retained.[10,11]

Any mechanism for desensitization must indicate some manner of interference with the process of latent image formation. Ultimately, a latent image results when an electron leaves the atmosphere of a bromide ion and combines with a silver ion. Neutral silver and bromine result from this transfer, although the electron which originally left the bromide ion may not be the same one which eventually combines with the silver ion. The energy which triggers this electron transfer is the exposing light.

Desensitizers generally do not interfere with the conductivity of an irradiated emulsion.[12] Therefore, it is believed that desensitizing agents are competitors for photoelectrons. The desensitizing dye successfully acquires the electron which would in normal circumstances lead to the formation of a latent image.

It is the purpose of this paper to show how desensitizers, operating in an "atmosphere" of silver ions in a photographic emulsion, can capture electrons. Although different organic structures exhibit desensitizing properties, these molecules show a basic similarity which explains their desensitizing or electron associating capabilities. Thus, these apparently different compounds are connected in their desensitizing ability.

Despite the fact that a molecule desensitizes and does not inhibit photoconductivity, it may do so without necessarily forming an association with the electron. A desensitizing agent can function by virtue of an ability to accept energy from an excited electron, while the electron returns to an unexcited state. The desensitizer, which likewise is now in an excited state, may dissipate its energy in a photographically useless manner. However, the desensitizing agents discussed here will be those which do not interfere with the mobility of excited electrons, which do not attack a latent image, and whose action is interpreted as an ability to form an associative combination with mobile electrons in the photographic emulsion. This action is competitive with the photographic trapping process.

It should be carefully pointed out that this paper does not delineate the *only* mechanism for desensitization. What is attempted here is the establishment of a relationship among some of the known structures, which may be one approach to explain desensitization. Naturally, it is hoped that this working hypothesis will lead others to experimental work. Of interest, for

* Ansco Research Laboratories, Binghamton, New York. Received January 31, 1955.

example, is the effect of pAg in connection with desensitizing action.

Position of Desensitizers in the Emulsion

It has been proposed that the desensitizers function well when they can function in close proximity to sensitivity specks.[9,13] This may be particularly evident in view of the ability of small concentrations of desensitizers to be so effective. Thus, they appear to operate in close contiguity with the sensitivity specks of the photographic emulsion and in this manner serve efficiently to trap the photoelectron which is released upon exposure. These traps function in a superior manner to the usual traps of the photographic process. However, the native, as well as the desensitizer traps are both insufficient for the inhibition of photoconductivity.

The mechanism of the trapping of an electron or the mode of accretion of silver ions to a trapping site need not be discussed here.[14] The desensitizers which function at these centers are in the presence of silver ions which occur at the sensitivity specks; either these ions are present there originally or arrive there by subsequent migratory processes. The discussion below, however, will fit equally well for desensitizers randomly distributed over the silver halide surface.

The ability of an unsaturated system to complex silver cations is well documented.[15,16] As depicted below, an unsaturated aliphatic system can be shown to complex silver cations by virtue of several resonance

forms which lend stability to the association. The ability of electronegative atoms, such as oxygen, to complex silver has also been reported.[17]

Similar to the olefin complexes above, silver·ion-aromatic nuclei associations have been described.[18,18a] Stabilization by forms of the type:

in which the silver ion is located above the plane and on the six fold symmetry axis of the ring, have been suggested as contributing to the resonance hybrid.[18b] Studies of some solid complexes,[19] with additional support from quantum mechanical considerations,[20] however, lead to the belief that the silver ion is located away from the symmetry axis, lying above and between two carbons of the aromatic ring.

For purposes of the present discussion it is not necessary to postulate the association of the silver cation with any specific atom of a dye (to form a sigma complex). Stable complexes with the unsaturation electrons may occur (pi complexes).[21] There is also no need to speculate as to the relative steric orientations of the donor and acceptor portions of the complexes discussed below.

Stable Odd Electron Systems

If a desensitizer is to function by virtue of its ability to form a complex with a mobile electron in the emulsion, while situated in a silver ion "atmosphere", it becomes apparent that an odd electron system or free radical results. It is instructive to consider some stable odd electronic configurations. In accordance with the treatment by Pauling, the ability of certain pairs of atoms to form stable bonds with an odd number of electrons can be explained by the application of quantum mechanics.[22] The stability of this odd electron bond arises from a resonance of the electrons between the two nuclei:

I   A: ·B
II A·   :B

Thus, the electrons can be introduced into the orbitals of the nuclei of atoms A or B in the manner shown above, since the exclusion principle of Pauli allows only two electrons of opposed spins in any one orbital. Now, neither structure I nor structure II corresponds to the actual stable structure of the molecule AB, which is bonded together by the three electrons. Such structures alone would lead to repulsion of the atoms, or at best a weak attraction. If atoms A and B are the same or nearly the same (i.e., they do not differ by more than ~0.5 in electronegativity) than resonance between structures I and II can occur, with a stable bond resulting. That is to say, if atoms A and B are not identical, they should be at least adjacent in the periodic table. This bond is about one-half as strong as the usual covalent bond formed by a pair of electrons. This theoretical approach to the stability of a three electron bond is essentially the same as for a one electron or a two electron (covalent) bond.

Only three electron systems are considered here since more complicated organic odd electron structures can be viewed as vinylogues of the system A $\cdots$ B discussed above.

These odd electron organic structures may arise by oxidative or reductive processes. Such structures may also arise by reduction, followed by oxidation.

A familiar example of an odd electron organic structure resulting from an oxidative process is the stable Wurster salt obtained by the oxidation of a p-phenylenediamine:
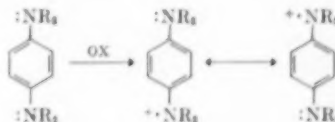

In this case there is a resonance between the equivalent nitrogen atoms which renders this odd electron system stable. There is also some contribution to the stability of the radical made by the forms:

69

These latter forms are less important, since the carbon atom is less able to carry the odd electron. As will be seen in the case of the cyanine and triphenylmethane dyes, if enough atoms are available for carrying the odd electron, then a radical of enhanced stability can be formed (i.e., if there is an increase in the number of canonical forms contributing to the resonance hybrid, the resonance energy of that structure will be greater).

Mention may be made of the fact that oxidized color developer (a p-phenylenediamine derivative) is known to effect desensitization of the photographic emulsion. We may have a Wurster salt of the above type being formed here by reduction in a one electron stage of the oxidized color developer. This removes the electron from the photographic process. However, Wurster salts are normally conceived as arising by a process of oxidation.

By the reduction, in a one electron stage, of γ,γ'-dipyridyl,

$$:N\!\!\bigcirc\!\!-\!\!\bigcirc\!\!N: \quad,$$
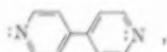
in acid media, or better by the reduction of γ,γ'-biquaternary dipyridylium compounds,

$$R\!-\!N\!\!\bigcirc\!\!-\!\!\bigcirc\!\!N\!-\!R \quad,$$

in either acid or alkaline solution, there are obtained odd electron systems of stability. This stability is believed to arise from resonance of the type:

$$\text{[structure diagram]} \longleftrightarrow \text{[structure diagram]}$$

with minor contributions from structures such as

$$\text{[structure diagram]} \quad \text{and} \quad \text{[structure diagram]}$$

Thus, γ,γ'-dipyridylium salts might be expected to desensitize an emulsion by virtue of their ability to be reduced in a one electron process to a stable product, if the reduction potential of the salt is of the right magnitude. Indeed, such compounds have been patented as desensitizers.[23]

The dye sensitized photopolymerizations described by Oster represent examples of free radicals formed first by a reduction which is then followed by an oxidation of this reduced form of the dye to a semiquinone or radical form.[24]

Subsequent discussion will indicate how a variety of different nuclei may be related by their ability to associate with an electron and thus desensitize a photographic emulsion. After association (that is, reduction) stable structures are assumed, which make the desensitizing action potent. In the ability to form these resonance stabilized structures, after association, the desensitizers are related.
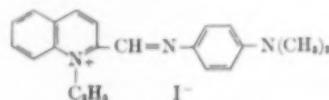
A large number of heterocyclic bases, of the quinoline, acridine, and phenazine series, are known to give products of a radical type by a one electron reduction mechanism. The photoelectron in the presence of a silver ion can be visualized as an "electrode" for such a process. If this be so, several corollaries follow: (1) For the desensitizer to be effective, i.e., reduced, it must be in close proximity to an electron and silver ion. Even in true electrode processes, one electron reductions occur at the electrode only.[25] (2) If the desensitizing action actually results in stable radical formation, then one may predict that as in some known radical reactions (e.g., polymerizations) there will be desensitizers which will function as chain inhibitors (cf. below under pinakryptol green).[24] This inhibition results from chain termination by molecules which yield highly stabilized resonance systems which do not react further. (3) If the desensitizing action is a one electron reduction to a free radical, then it ought not to be a function of the oxygen content of the system. The enhancement of densensitization by oxygen has been shown to be small.[26] (4) A final consequent of a radical mechanism for desensitization should be the increased stability of the resonance hybrid by contributions from forms with the odd electron on atoms of different electronegativities, as the multiplicity of such forms increase (vide infra cyanine desensitizers).

Azacyanine Desensitizers

These are dyes in which a $-CH=$ of the methine chain of a cyanine has been replaced by nitrogen. It is, perhaps, proper to start with these compounds since they appear to be sensitizing dyes, yet are actually desensitizers. Kendall has pointed out that

$$\text{[structure]} CH\!=\!CH\!\!-\!\!\bigcirc\!\!-\!\!N(CH_3)_2 \quad I^-$$
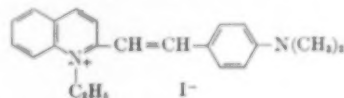
was a sensitizing dye, whereas,

$$\text{[structure]} CH\!=\!N\!\!-\!\!\bigcirc\!\!-\!\!N(CH_3)_2 \quad I^-$$

was a desensitizer.[10] Kendall was the first to call attention to the fact that the number of carbon atoms separating the terminal nitrogen atoms in the chromophoric chain in the resulting molecule was the deciding factor in determining whether substitution of $-N=$ for $-CH=$ would provide a sensitizer or a desensitizer.[11]

Stated generally, desensitizing structures have an even number of conjugated methine groups connecting electron withdrawing atoms. As a result of quantum me-

chanical resonance in the ground state of the desensitizer molecule or ion the electron withdrawing atoms are capable of delocalizing the electron pairs and decreasing the electron density in the attached conjugated system.

This type of phenomenon may be more clearly demonstrated in the case of the symmetrical thiacarbocyanine sensitizer.
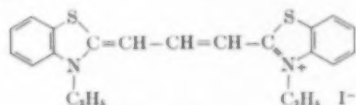

Replacement of the central (or meso) methine group by a nitrogen atom provides the desensitizer,
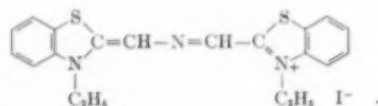
This desensitizer has an even number of carbon atoms between the central nitrogen and the two terminal nitrogens. In this example, a sensitizing dye is converted into a desensitizing dye.

If the incoming nitrogen atom does not replace the meso —CH= group, the resulting molecule,
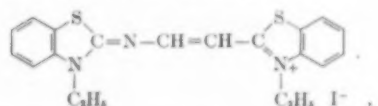

contains an odd number of carbon atoms between the replacing nitrogen atom and the end nitrogens. A sensitizing dye then results; of course, accompanied by spectral changes. Since the structure formed produces a molecule which retains intact an amidinium structure, $\left(\diagdown N-(CH=CH)_n-CH=\overset{\cdot\cdot}{N}\diagup \right)$, it is not surprising that it is a sensitizer. What is believed to occur is that the incoming nitrogen atom partakes of amidinium ion resonance with each of the terminal nitrogens. Such resonance is required for a dye to be a photographic sensitizing dye of the cyanine type. This does not, however, explain the desensitization obtained by replacement of the middle methine group of the conjugated chain.

An explanation can be attempted in the following manner: Extending the cyanine chain (getting the next higher vinylogue) and replacing the middle —CH= by a nitrogen (to give a desensitizer) we can picture several resonance forms of this molecule before it associates with a silver ion and an electron.
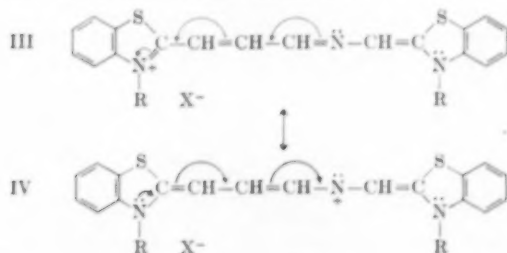
We may ascribe desensitization to the ability of this compound (of which forms III and IV contribute to the hybrid) to associate with an electron, before the electron can combine with a silver ion in the photographic emulsion. This we do since desensitizers, azacyanines included, do not inhibit photoconductivity. In the following is shown such a combination of the azacyanine with a silver ion and the electron: •
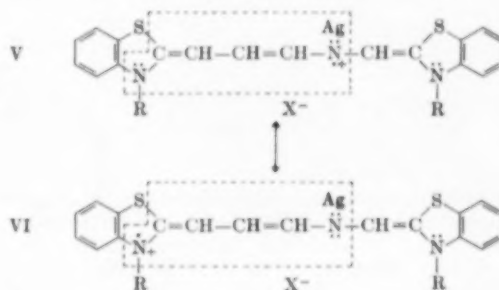

Forms V and VI represent the more stable forms of the dye in association with the electron and silver ion. Other resonance forms have been omitted. Desensitization can be pictured in this fashion. The electron and silver ion addition, as shown above and subsequently, is depicted on specific atoms. Although this is convenient, *it is only symbolic*. The resonance forms, in the dotted lines, appear identical to the resonance forms in the case of the Wurster salts or the reduced γ,γ'-dipyridylium salts, representative of stable odd electron systems. Such stability seems to occur when there is an even number of conjugated carbons separating the nitrogens. This explains why substitution of a nitrogen in the center of the methine chain of a cyanine gives rise to a desensitizer. The resulting structure is stabilized by resonance.

Azine Desensitizers

In this series can be found some of the best examples of desensitizing dyes. The one used commercially, pinakryptol green, is a good illustration. In this case again, an electron and silver ion can be in stable association with the desensitizing dye.

Below are shown two of the many resonance forms for pinakryptol green:

(structures IX, X, XI, XII)
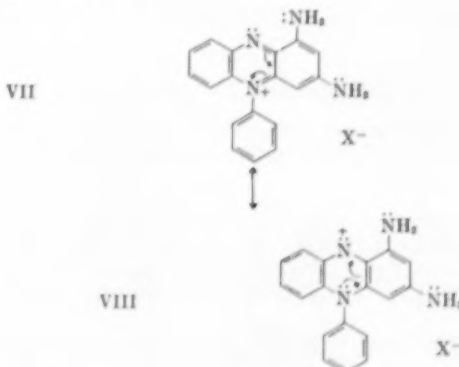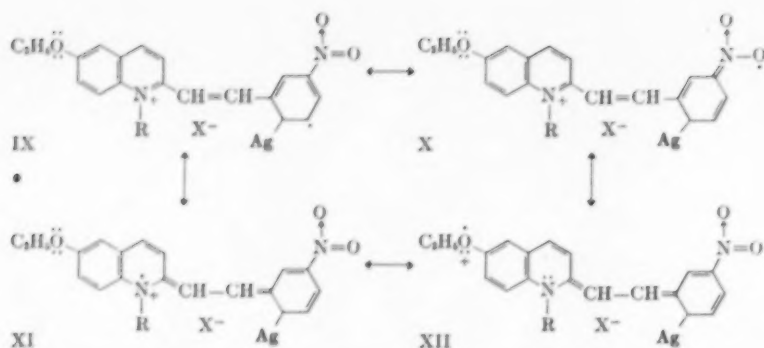
The more stable resonance structures for pinakryptol green, acting as a desensitizer, are shown as follows:
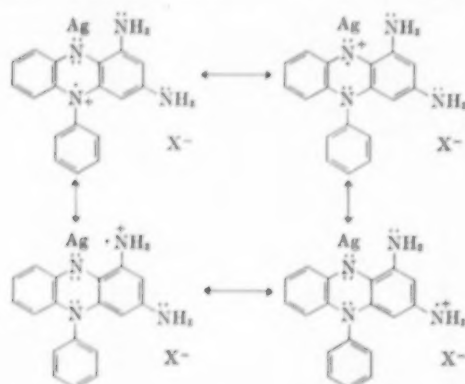
The ability of phenazines to become associated with an electron to give a radical is well known from polarographic studies. These studies indicate that reduction of phenazine nuclei frequently occurs in a one electron stage. Additional evidence for the stability of such free radicals comes from the fact that azine dyes, particularly pinakryptol green, even in trace amounts (10^{-8} percent) are inhibitors of dye sensitized photopolymerizations as described by Oster.[24] This ability to inhibit or anticatalyze a radical reaction process is a characteristic of a very stable free radical system. Such inhibitors (or stabilizers) are, in the case of organic compounds, structures which can yield stabilized resonance systems.

Styryl Structures as Desensitizers

The example par excellence of this class of sensitizing dyes is pinakryptol yellow which has the structure:
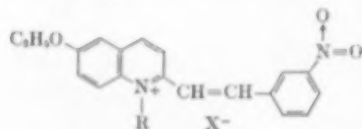
Here the addition of an odd electron and a silver ion give rise to a variety of structures stabilized by reso-

nance. Suitably placed nitro and ether groups are well known to stabilize free radicals.[27] The additional electronegative nitrogen and oxygen may carry the odd electron easier than a carbon atom. Further, since the electronegativities of the oxygen and nitrogen atoms do not differ widely, important resonance stabilization to this hybrid may be obtained by resonance between these forms, since they are almost completely degenerate (structures X, XI and XII). This may be diagrammed as shown above:

Anthraquinone Desensitizers

A class of desensitizers possessing structures differing from those mentioned previously are the anthraquinones. Such compounds as anthraquinone-2-sulfonic acid and 1-chloroanthraquinone-2-carboxylic acid have been patented for this purpose.[28]

It is instructive to include the anthraquinones although it must be mentioned that their desensitizing action has been ascribed to the ability of these compounds to form insoluble complexes with cyanine type sensitizing dyes. Emulsions sensitized with acid dyes (e.g., erythrosin) are reported as being unaffected by anthraquinone desensitizers. Such acid dyes form no insoluble complexes with the desensitizer. Further evidence adduced to the above view for the mode of action of anthraquinone derivatives is the failure of this class of desensitizers to catalyze the Herschel effect.[29]

Using anthraquinone itself it would appear that the following electronic displacement might occur:
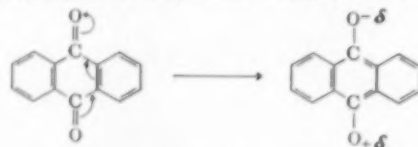
Addition of an electron in the presence of a silver ion would yield an odd electron molecule having the configuration:
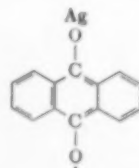
Similar structures, classified as free radicals of long life, are known. Such are,[30,31]

and

Structures prepared by Knott, which may be compared to the anthraquinones (dotted lines) and which embody the requirements for a desensitizer as defined by Kendall are of the type:

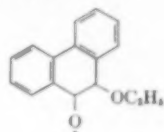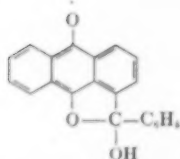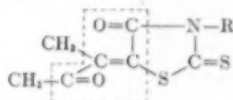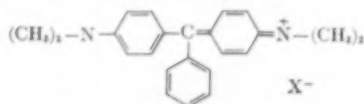Since these molecules possess two electron withdrawing groups connected by an even number of conjugated carbons, Knott expected that they would be strong photographic desensitizers. They are.[32]

Triphenylmethane Desensitizers

Such a desensitizing dye structure is particularly exemplified by malachite green,

in which there is a resonance hybrid contribution to the ground state by the form,
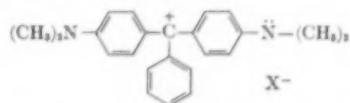

Addition of an electron in the presence of a silver ion to the dye would produce a structure entirely analogous to the well known stable triphenylmethyl radical, in which resonance occurs among forty-four canonical states. This structure may be represented as
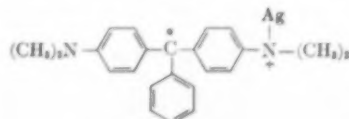
It is of interest that malachite green contains conjugation analogous to the cyanine system, with a phenyl group on the meso carbon. It is, nevertheless, not sur-

prising that this compound is a desensitizer. Stabilization of free radicals by resonance in the triphenylmethanes appears to be the more powerful influence. Of interest is the comparison of malachite green to its counterpart, a true cyanine dye with a meso phenyl group, e.g.,
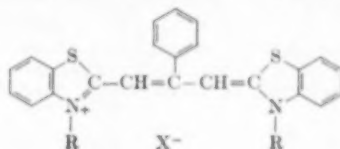
This 9-phenylthiacarbocyanine is a sensitizing dye.

A fundamental difference may exist between the 9-phenylthiacarbocyanine and malachite green. It has been suggested that the phenyl group in the meso position of the thiacarbocyanine is not coplanar with the remainder of the molecule.[33] Plain projections of 9-phenylthiacarbocyanine indicate that there would be severe crowding of the hydrogen on the phenyl and the heterocyclic sulphur if the molecule was entirely coplanar. For resonance stabilization of a free radical it is believed that coplanarity is necessary for all the participating groups. It has been assumed that this coplanarity is sufficiently achieved by the triphenylmethyl radical to render it stable.[34] However, it is true that complete coplanarity does not appear possible in triphenylmethyl since that would require the ortho hydrogens of the different phenyl groups to lie too close together.[35]

Cyanine Desensitizers

In addition to the desensitizing dyes listed above, many cyanine dyes themselves exhibit desensitizing properties. This action, to the native emulsion response and to the induced sensitivity response, has been shown to be independent of the sensitizing action of the dye.[?]

Actually, all cyanines can exhibit free radical stabilization by resonance in a manner similar to that shown by the desensitizing azacyanines discussed above. Resonance stabilization in this case is attained by contributions from forms in which the odd electron is located on carbon and nitrogen atoms.
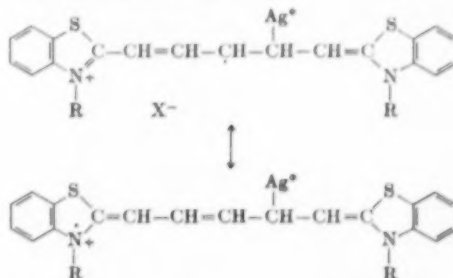
Such forms differing in electronegativities will contribute less than identical or more nearly degenerate forms.

As mentioned above, as the number of resonance forms composing the radical hybrid increases its stability in-

---

* Again, the electron and silver ion addition is depicted on specific atoms for convenience only and should be regarded as merely symbolic.

creases; that is of course, its thermochemical stability. The assumption that greater stability is achieved by a hybrid molecule if it resonates among an increased number of contributing classical structures has been shown to have correspondence in the molecular orbital theory.[36] Thus, a vinylogue of a desensitizing structure should, all other things being equal, exhibit even further desensitizing powers, as a result of contributions to the radical hybrid by an increased number of canonical forms, albeit, the forms may not be identical (i.e., incomplete degeneracy).

Further, the contribution of any particular unexcited canonical form may be greater than any single excited form. However, this effect may be outweighed by a greater number of the excited (or ionic) forms. For polycyclic naphthacene the unexcited canonical forms appear to make virtually no contribution.[37] Indeed, it has been recognized that a number of heterocyclic ring systems exist for which no classical structure, using normal covalent linkages, can be written. This has led W. Baker and his colleagues[38] to call these mesionic compounds; a $\pm$ formulation is used to represent the aromatic-type hybrid structures obtained from the large number of contributing ionic forms.

Focusing attention on the cationic portion of a cyanine dye, the following structures exemplify the kind of stabilization by resonance among ionic forms the dye may achieve after it associates with an electron:
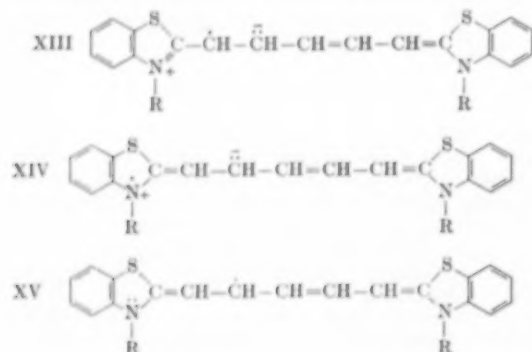

Structures XIV and XV resemble those shown as minor contributors to the free radical formed by the one electron reduction of γ,γ'-biquaternary dipyridylium compounds.

Whatever the operative mechanism, it appears that as the cyanine dyes are converted to their higher homologues they become more potent desensitizers—so that di- and tricarbocyanine dyes can be used only in small concentrations because of their rather high desensitizing action.[2,39] With infrared dyes desensitization appears to be the dominating factor.

In practice, silver halide emulsions are desensitized by additions of any of a number of cyanine dyes. Higher concentrations desensitize the induced ranges, while the native response of the emulsion decreases even with small additions. On the contrary, some cyanine dyes have been shown to be without desensitizing action (over and above filter action) when added in large amounts to an emulsion.[2,40] Supersensitizers have been shown to decrease the desensitizing action in some instances.[40]

Spence and Carroll have pointed out that 3,3' diethyl-thiacarbocyanine iodide,
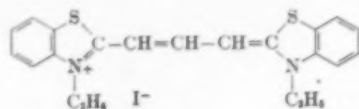
and 3,3'-diethyl-4,4'-diphenylthiazolocarbocyanine iodide,
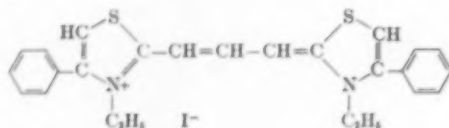
have similar structures and similar distributions of optical sensitization.[2] The former is a good sensitizer while the desensitizing property of the latter is as powerful as that of pinakryptol green.

Restricting attention to the thazolo portion of the latter dye, addition of an electron in the presence of a silver ion results in a structure which is capable of the following resonance:
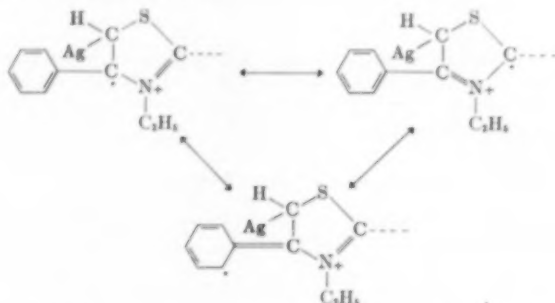
In this case resonance stabilization of the radical is achieved by structures where carbon atoms bear the odd electron.

Conclusion

Desensitization can be viewed as a diversion of mobile electrons from latent image formation. Many different organic structures function as desensitizers for the photographic process. The action of these structures can be related by assuming that they accept or are reduced by a mobile electron prior to its combination with a silver ion. A silver ion and an electron serve as "electrodes" for the reduction of the desensitizers. Desensitizers appear similar in that the final structures formed upon reduction, which are radicals, are capable of resonance stabilization.

References

1. J. M. Eder, Sitaber. Akad. Wiss. Wien, math-phys. Klasse, Vol. 90, p. 1097 (1884); Ausführliches Handbuch der Photographie, 5th Edition, Vol. 3, p. 152, W. Knapp, Halle (1903).
2. J. Spence and B. H. Carroll, J. Phys. and Colloid. Chem., Vol. 52, p. 1090 (1948).
3. M. Blau and H. Wambacher, Z. wiss. Phot., Vol. 33, p. 191 (1934).

4. B. H. Carroll, J. Phys. Chem., Vol. 29, p. 693 (1925).
5. B. H. Carroll and C. M. Kretchman, Bur. Stand. J. Res., Research Paper No. 541, Volume 10, p. 449 (1933).
6. G. O. Schenck, et al., Ann., Vol. 584, pp. 125-238 (1954).
7. K. Weber, Z. wiss Phot., Volume 35, p. 124 (1936); Vol. 36, p. 1 (1937); Phot. Korr., Vol. 63, p. 42 (1932); Vol. 71, p. 107 (1935).
8. C. E. K. Mees, "The Theory of the Photographic Process," Revised Edition, 1954, p. 425.
9. M. Tamura and S. Tutihasi, Royal Photographic Society Centenary, London, Sept. 1953, uncorrected preprint.
10. J. D. Kendall, Brit. Pat. 447,109 (1936).
11. J. D. Kendall, Int. Congr. Photography, Paris, 1935.
12. W. West, "Fundamental Mechanisms of Photographic Sensitivity," Butterworths Scientific Publication, London, 1951, p. 99.
13. A. Hautot and H. Sauvenier, Collogue Sur La Sensibilité Des Cristaux Et Des Émulsions Photographiques, Paris, Sept. 1951, Sci. et Ind. Phot., Vol. 23, p. 137 (1951).
14. For pertinent later views see J. W. Mitchell, J. Phot. Sci., Vol. 1, p. 110 (1953).
15. S. Winstein and H. J. Lucas, J.A.C.S., Vol. 60, p. 836 (1938).
16. H. J. Lucas, R. S. Moore, and D. Pressman, J.A.C.S., Vol. 65, p. 227 (1943).
17. A. E. Comyns and H. J. Lucas, J.A.C.S., Vol. 76, p. 1019 (1954).
18a. L. J. Andrews and R. M. Keefer, J.A.C.S., Vol. 71, p. 3644 (1949).
18b. H. J. Taufen, M. J. Murray, and F. J. Cleveland, J.A.C.S., Vol. 63, p. 3502 (1941).
19. R. E. Rundle and J. H. Goring, J.A.C.S., Vol. 72, p. 5337 (1950).
20. R. F. Mulliken, J.A.C.S., Vol. 74, p. 811 (1952).
21. M. J. S. Dewar, J. Chem. Soc., p. 406, 777 (1946).
22. L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., (1942).

23. Brit. Pat. 714,290 (8/25/1954).
24. G. Oster, Nature, Vol. 173, p. 300 (1954); Phot. Engineering, Vol. 4, No. 3, p. 173 (1953).
25. P. J. Hillson and E. Rideal, Proc. Roy. Soc., Vol. A 216, p. 458 (1953).
26. W. Vanselow, R. E. Quirk, and B. H. Carroll, Phot. Sci. and Tech., Vol. 18, No. 3 (1952).
27. G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, 1944, p. 324.
28. U. S. Patents: 1,753,911 (1930); 2,131,742 (1938); 2,132,169 (1938); 2,172,192 (1939).
29. F. M. Hamer, N. I. Fisher, and E. M. Leeson; Int. Congr. Photography, Dresden, (1931).
30. S. Foldschmidt, A. Vogt, and M. A. Bredig, Ann., Vol. 445, p. 123 (1925).
31. L. F. Fieser and W. Y. Young, J.A.C.S., Vol. 54, p. 4095 (1932).
32. E. B. Knott, J. Chem. Soc., 1490 (1954).
33. P. Bruylants, A. Van Dormael, and J. Nys, Bull. Ac. R. Belg., Vol. 34, p. 703 (1948); cf. also, L. G. S. Brooker, F. L. White, D. H. Heseltine, G. H. Keyes, S. G. Dent, Jr. and E. G. Van Lare, J. Phot. Sci., Vol. 1, p. 173 (1953).
34. E. S. Wallis and F. H. Adams, J.A.C.S., Vol. 55, p. 3838 (1933).
35. G. Karagunis and G. Drikos, Naturwissenschaften, Vol. 21, p. 607 (1933); Nature, Vol. 132, p. 354 (1933); Z. Physik. Chem., Vol. B26, p. 428 (1934).
36. M. J. S. Dewar and H. C. Longuet-Higgins, Proc. Roy. Soc., Vol. A, 214, p. 482 (1952).
37. A. Pullman and B. Pullman, Experientia, Vol. 2A, p. 364 (1946).
38. Ann. Reports on the Progress of Chemistry for 1951; Vol. xlviii, The Chemical Society, London p. 213 and references therein.
39. H. O. Dickinson, J. Phot. Sci., Vol. 2, p. 50 (1954).
40. Unpublished experiments by the authors.

SOME PROBLEMS IN THE PRODUCTION OF MULTIPLE COPIES BY THE DIFFUSION TRANSFER PROCESS

A. J. Sievers*

THE PRODUCTION of more than one positive from a single negative by means of the diffusion transfer process has long been desired and considered feasible. For example, A. Rott in German patent number 764,572 dated July 10, 1940, mentions this possibility. However, to date none of the companies marketing processes of this type offer this advantage. Following is a description of the principles involved in this type of process.

A slow speed contact emulsion, preferably of the reflex type is exposed to the material to be reproduced. It is then passed into the processing solution together with a specially prepared "positive" sheet of paper. After both sheets have been immersed in the solution, they are pressed into intimate contact by a pair of pressure rollers which also squeegee off the excess solution as the prints are passed out of the processing machine in a semi-dry condition. After approximately 20 seconds have elapsed, the negative and positive sheet are stripped apart and the positive allowed to air dry for a few minutes, after which time it is ready for use. The nega-

tive is now ordinarily discarded, but it may be washed and dried for future use by conventional photographic means.

The processing solution consists of the reducing agent, a preservative, an alkali, a restrainer and a silver halide solvent. The reducing agents are selected on the basis of rapid reduction of the exposed silver halide since the paper is immersed in the processing solution for only approximately 12 seconds. The combinations in general use today are the Metol or Phenidone†-hydroquinone combinations. Sodium sulfite, potassium metabisulfite or, in some instances, a combination of both are the generally used preservatives. Since rapid reduction of the exposed silver halide is necessary, sodium hydroxide is most usually employed as the alkali and this is used in amounts to yield a working pH of approximately 11.0–12.0. As restrainers, either the well known inorganic ones such as potassium bromide are used or the organic heterocyclics: benzotriazole, 6-nitro benzimidazole, etc., are employed. The latter ones have the added advantage of also acting as "blue-black" agents and in most cases this is desirable. However, a combination of the inorganic and organic restrainers may also be used. For the silver solvent, sodium thiosulfate

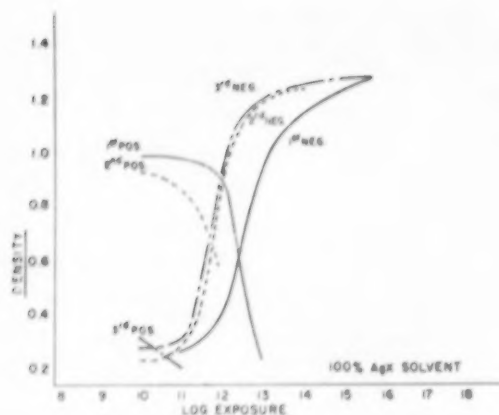† Trademark of Ilford, Ltd., for 1-phenyl-3-pyrazolidone.

Fig. 1. Sensitometric curves for a processing solution having a 100% silver halide solvent content. It shows the relative positions of the positive curves obtained for 3 successive copies, together with their corresponding negative curves. ——— 1st copy, --------- 2nd copy, ----- 3rd copy.

(hypo) is most universally used; although, the more expensive and also more active ammonium thiosulfate is also finding use, usually in combination with the sodium hypo.

In the transfer process the silver solvent works in exactly the same manner as a conventional fixing bath. It solubilizes the unexposed and therefore undeveloped silver halide of the negative emulsion by reacting with it to form, in the case of sodium thiosulfate for example, a silver thiosulfate complex.

Once solubilized, the negative silver halide (which represents a positive image of the original subject matter) is now capable of migrating across the liquid interface between the negative and positive sheets. The positive sheet has a surface coating which may consist of gelatin or resin usually containing reduction nuclei and acts as a surface for formation of the positive image.
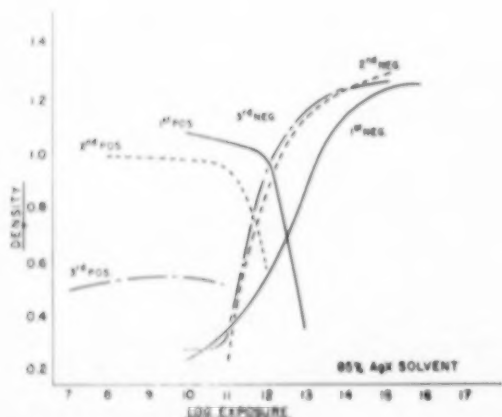
Fig. 2. Same as Fig. 1 but for a processing solution having an 85% silver halide solvent content.

Possibility of Multiple Copies

The limiting factor in producing multiple copies from one negative might appear to be a lack of sufficient negative silver halide in the unexposed and undeveloped areas. However, when a determination was made of the amount of silver halide contained in a given area of negative emulsion and a similar determination was made of the positive image transferred from this same area, it was found that only 14.0% of the available negative silver halide had been deposited upon the receptive layer. This 14% was equivalent to a positive density of 1.0 at 30 seconds contact time and 68 F. Theoretically there should be sufficient silver halide present in the negative to make seven copies.
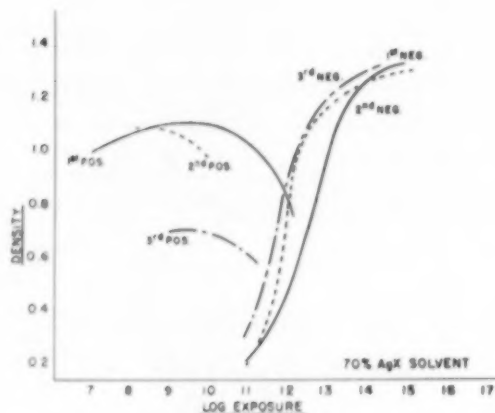
Fig. 3. Same as Fig. 1 but for a processing solution having a 70% silver halide solvent content.

Conditions Unfavorable to the Formation of Multiple Copies

When an attempt was made to form a second copy by passing the negative sheet through the developing machine a second time with a new sheet of receptive material, either no image at all or at best an unacceptable one was received. Since analysis had shown the presence of sufficient silver halide for a second copy and since the processing solution contained ample silver halide solvent to transport this remaining silver halide to the positive sheet, there must still be other factors to be considered. A rapid reduction of the remaining silver halide to metallic silver in the form of negative fog would make this silver halide unavailable for transfer. Simple densitometric measurements of various fog densities together with analysis to determine the corresponding amounts of silver showed that only a very small proportion of the remaining silver halide was made unavailable for transfer by fog formation. Still another factor might be a rate unbalance between the several reactions which occur almost simultaneously during the processing step. Since these reactions are all in competition for the limited amount of silver halide present, anything but a precise chronological sequence between them would re-

PHOTOGRAPHY
IN SCIENCE

11TH OPEN EXHIBIT OF TECHNICAL PHOTOGRAPHY
1955 PSA INTERNATIONAL EXHIBITION
OF PHOTOGRAPHY · OCTOBER 5–8 · SHERATON PLAZA HOTEL · BOSTON, MASS.

To show the use of photography today in science, the Photographic Society of America announces an exhibit, to be shown at the Society's Annual Convention and later throughout the United States.

The Technical Division of the PSA needs your best photographs to make this exhibit outstanding.

Any photograph taken for scientific purposes is eligible.

Read the simple conditions in this folder and send your photographs to arrive on or before August 25, 1955 to:

PSA TECHNICAL DIVISION EXHIBIT · GEORGE EASTMAN HOUSE · 900 EAST AVENUE · ROCHESTER 7, NEW YORK

CONDITIONS OF ENTRY

The Technical Division of the PSA is pleased to announce that this year the exhibit will be designed by the George Eastman House in conformity to the best display practices. The photographs will be mounted on uniform 16 × 20-inch boards and the descriptive material will be printed in a uniform typographical style. For this reason prints must be submitted unmounted.

---

1 Entry is open to anyone, anywhere. Membership in the Photographic Society of America is not a requirement.

2 No entry fee is required.

3 Any type of subject matter may be chosen which utilizes industrial or scientific photography. Purely pictorial photographs of equipment or mechanical operations however will not be accepted. Practical applications of photography to technical problems are desired as well as photographs that in themselves reveal new scientific knowledge of general interest. Photographs in such varied fields as armament, agriculture, astronomy, geology, medicine and physics are welcomed. However, photographs in the fields of zoology and botany except photomicrographs should generally be entered in the PSA Nature Division Exhibit.

4 Both black-and-white and color prints, and transparencies $2^1/_4 \times 3^1/_4$ inches or larger by any photographic process are acceptable.

5 Prints must be sent *unmounted*, accompanied by descriptive material explaining the purpose of each picture and how it was made. All photographs selected for the exhibition will be mounted by the George Eastman House, and the labels will be edited from your copy. The maker's name and his company affiliation (if any) will be clearly indicated.

6 The contributor's name and address should appear on the back of each photograph and on the mount of each transparency. Each print should be numbered and separate descriptive material given the same number.

7 There is no limit on the number of prints or transparencies that may be submitted by a contributor.

8 While all possible care will be taken to safeguard prints and transparencies, neither the Society nor the Exhibition Committee can assume any responsibility for loss or damage.

9 For your convenience and the protection of your photographs we have included an address form which may be pasted on the package containing your entries. Please use this form to mail your photographs to the George Eastman House, 900 East Avenue, Rochester 7, New York.

10 All contributors are requested to complete the accompanying entry form and mail it to Henry J. Fassbender, 36 Couchman Avenue, Rochester 17, New York.

11 Acceptance for the Exhibit will be determined by a panel of three judges. All contributors will be notified of acceptances or rejections immediately after the judging. Further selection of photographs for the Technical Division's Travelling Exhibits or PSA Invitational Exhibition will be made after the convention with notification given at that time. All photographs not included in one of these additional exhibits will be returned after the close of the convention.

12 Each contributor will receive an illustrated catalog of the 1955 PSA International Exhibition.

ENTRY FORM
PSA TECHNICAL EXHIBIT 1955

All contributors are requested to complete this form and send it by 1st Class mail to Henry J. Fassbender, 36 Couchman Ave., Rochester 17, New York. Please do NOT enclose this form with your prints or transparencies.

Exhibitor's

Date _____

Name _____ Occupation _____

Last   First   Initial

Street Address _____

City _____ Zone _____ State _____

Company Affiliation _____

Please check (√) appropriate columns or boxes

TITLE OF PHOTOGRAPH	Print	Transparency	Permission is granted to retain this photograph up to 2 years if selected for the Technical Division Traveling Exhibits or PSA Invitational Exhibition			
1			Yes		No	
2			Yes		No	
3			Yes		No	
4			Yes		No	
			Yes		No	
			Yes		No	

Permission is also granted to reproduce prints and/or transparencies for publicity purposes in connection with the exhibits.

Remarks _____

Signature _____

Cut here

PERSONAL RECORD

Retain this part for your files

Eleventh Open Exhibit of
Technical Photography
1955 PSA
International Exhibition
Boston, Mass.

This entry was selected for

Title of Photograph	Technical Exhibit	Technical Division Traveling Exhibit	PSA Invitational Exhibition
1			
2			
3			
4			

For Mailing All Photographs

cut here

cut here

From

To:

PSA Technical Division Exhibit

George Eastman House

900 East Avenue

Rochester 7, New York

CONTENTS. Photographs for exhibition only. Do not bend. To be returned to sender. May be opened for postal inspection.

11th OPEN EXHIBIT OF TECHNICAL PHOTOGRAPHY
1955 PSA INTERNATIONAL EXHIBITION OF PHOTOGRAPHY

CLOSING DATE Aug. 25, 1955
JUDGING DATE Sept. 7, 1955

11TH OPEN EXHIBIT OF
TECHNICAL PHOTOGRAPHY

JUDGES:

John Beiter, FPSA
Walter Clark, FPSA
Arthur Neumer

PSA TECHNICAL DIVISION EXHIBITION COMMITTEE

William Crain	Chairman
Paul Arnold, APSA, Hon. PSA	Committee
John Englert	Committee
Henry Fassbender	Committee
Eugene Fuerst	Committee
Hutson Howell	Committee
Beaumont Newhall, FPSA	Committee
Nathan Rickless	Committee
William Swann, APSA	Committee

SECTION REPRESENTATIVES

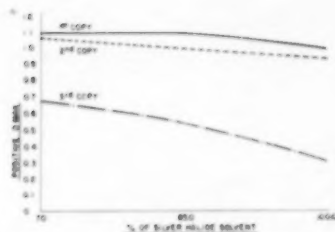|	
I. B. Current	Binghamton
H. Howell	Boston
P. B. Davis	Cleveland
H. Lyon	Ithaca
H. Croix	New York
D. Grim	Rochester

Fig. 4. The D. max values of the three positive copies in Fig. 1 and 3 are plotted against the range of silver halide solvent investigated.

sult in a waste of silver halide. For example, if the reduction of the exposed silver halide were not rapid enough or if the action of the solvent was too rapid so that both exposed and unexposed areas were attacked, an overall deposit of metallic silver would occur on the positive sheet. This would yield gray highlights and could only be corrected by increased exposure which, of course, would mean wasted silver halide. Or, if the solvent removed more silver halide than could be successfully reduced, silver halide would be wasted.

In an attempt to investigate all the possible factors, developer formulations were made covering all possible variations of component parts. The development rate was increased by means of development accelerating compounds, the pH adjusted; and the restrainer was investigated as to type and amounts. Two copies were obtained as a result of these studies. Silver analysis of the negative material, both before and after transfer, and analysis of the positive image showed that of all the possible limiting factors the action of the silver halide solvent was by far the greatest. While the processing solution was removing 52.1% of the available silver halide in the negative, only 26.8% was actually reduced on the positive sheet. That meant that 25.3% was lost to the processing solution; almost twice the amount required for formation of a positive image. Also 47.9% of the silver halide was left in the negative; enough to form another 3.4 copies. From these figures it became obvious that more detailed information concerning the role of the silver halide solvent was necessary.
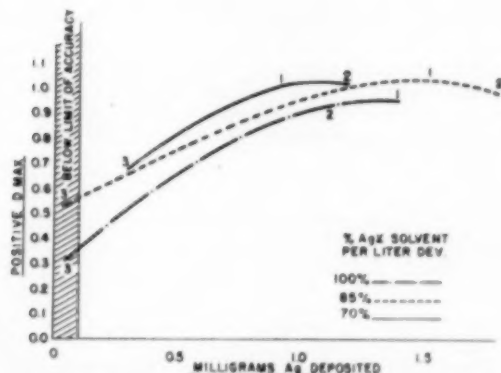

Fig. 5. The amount of metallic silver deposited to form the positive image and the maximum density produced by this amount for each of the three copies obtained in the three processing solutions investigated.

Processing solutions containing decreasing amounts of silver halide solvent were, therefore, investigated. A 25 sq. in. area of negative emulsion containing a known amount of silver halide was then exposed to a step wedge and a transfer print made in the usual manner. This was done for three solutions; each of different silver halide solvent concentration. Upon separating the positive sheet, the negative was immediately immersed in a stop bath and then washed. When dry, densitometric measurements were made of both sheets followed by silver analysis. The analysis of the negative material showed the silver halide equivalent of metallic silver in the exposed areas of the wedge and the amount of silver halide in the unexposed areas. Subtraction of
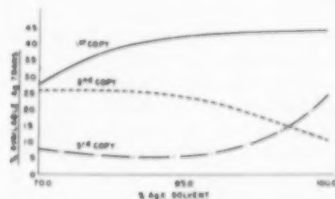
Fig. 6. The relationship between the percent of available negative silver halide transferred by varying concentrations of silver halide solvent is established for each of the three copies obtained.

this amount from the total silver halide content of the negative yielded the amount of silver halide removed by the solvent. To determine this amount as a percentage of the total silver halide available for transfer, it was necessary to determine the amount of original silver halide consumed to form metallic silver. This was done by exposing and transferring a negative wedge as before, but, this time, after separation of the sheets, the negative was "fixed" in a normal F-5 fixing bath. Analysis now yielded the amount of metallic silver required to form the negative wedge. Subtraction of the silver halide equivalent of this amount from the total silver halide gave the amount available for transfer. Analysis of the corresponding positive wedges showed the amount of this transferred silver halide actually deposited to form the final image.

Since the amount of available silver halide remaining in the negative after formation of the first copy was known, a second transfer was made. New negative and positive sheets were exposed and transfers made as before, saving the first copy and analyzing the second copy. Sensitometric values of the first copy compared to the measurements of the previous first set provided a check upon the accuracy and reproducibility of this method. After computing these results, a third transfer was made and analyzed by again taking new negative and positive sheets, setting aside the first and second copies for "checks" and analyzing the third negative and positive wedges.

Eight silver analyses were required to obtain a complete picture of the path of the silver halide throughout the process of forming three copies. From the H&D curves shown in Figure one, the effect of various amounts of silver halide solvent upon the production of multiple

copies can be seen quite clearly, especially for the third copy.

As shown in Figure one, the density vs. log exposure curve was obtained with a processing solution having a silver halide solvent content equivalent to standard single copy processing solutions. This amount was designated as 100% silver halide solvent.

Subsequent reductions, therefore, represent percentage decreases of this amount. Corresponding positive and negative curves have been plotted for the three copies obtained. As indicated, the maximum density of the third positive curve is approximately 0.3.

The series of curves in Figure two was obtained for an identical processing solution with the exception that the content of silver halide solvent was reduced by 15%. The negative curves are essentially the same but the densities of the three positive curves have all increased, especially the maximum density of the third copy which is now approximately 0.55.

As shown in Figure three, with a 30% reduction of silver halide solvent the negative curves remain essentially unchanged but the maximum density values of the positives are at a higher level. The third copy has been increased to a maximum density of 0.68.

Figure four shows the inverse relationship between positive density and percent silver halide solvent a little more clearly. The three slopes show that the greatest density increase occurs in the third copy.

Figure five shows the amount of silver deposited and the resultant densities for each of the three copies. The three curves represent the different percentages of silver halide solvents investigated. The three numbers on each curve are the values for each of the three copies obtained in that particular processing solution. In the second and third copies the density increases as the percent of silver halide solvent decreases, however, for the first copy the maximum density is essentially the same for the processing solutions having silver halide solvent concentrations of 70% and 85%.

In Figure six the relationship between the percent of silver halide solvent present in the processing solution and the percent of the available negative silver halide which is removed from the negative by transfer for each of the three copies can readily be seen. In the case of the first copy, the curve obtained is what one would expect; namely, an increasing amount of silver halide is transferred as the amount of silver halide solvent in the processing solution is increased. The curves for the second and third copies show a very interesting relationship, especially in the higher concentrations of silver halide solvent.

Table I

	70% AgX Solvent	85% AgX Solvent	100% AgX Solvent
1st Copy	27.5	42.7	44
2nd Copy	25.6	23.5	11.7
3rd Copy	7.8	5.7	23.5
	60.9	71.9	79.2
or approximately	60%	70%	80%

As shown in Table one and Figure six, transfer of the negative silver halide and subsequent image formation is most efficiently accomplished in the production of the second copy. Of the available negative silver halide, 25.6% is removed from the negative by the processing solution containing 70% silver halide solvent and results in the maximum positive density, while only 11.7% is removed from the negative by the solution containing 100% silver halide solvent. However, for the formation of multiple copies, maximum positive density is not necessarily proportional to maximum amount of silver halide removed from the negative. Referring to Figure four and Table one, the maximum density of the first copy is approximately the same for the processing solutions containing 70% and 85% silver halide solvent although the amounts of available negative silver halide removed are respectively 27.5% and 42.7%.

For the third copy the maximum density occurs for the 70% silver halide solvent concentration. This removes only 7.8% of the available silver halide as compared to 23.5% removed by the solution containing 100% silver halide solvent. As also shown in Figure four, the highest D max. for all three copies occurs for the processing solution containing 70% silver halide solvent. Table one shows this solution also removes only 60.9% of the available silver halide for the formation of 3 copies, while the other two solutions remove progressively more; namely, 71.9 and 79.2%. Hence, the solution with the lowest silver halide solvent concentration removes less silver halide from the negative after forming 3 copies than do the other two solutions. Theoretically the possibility of producing even additional copies with the three solutions tested is therefore greatest with the solution containing the least amount of silver halide solvent.

This entire investigation was based upon a standard contact time of 30 seconds for each of the three copies. Because of a difference in transfer rates, the densities shown for the three copies have diminished progressively with the number of copies. However, by using different contact times for each of the three copies, the densities can be matched quite nicely.

SOME PHOTOGRAPHIC COPYING METHODS
USEFUL IN LIBRARIES

Karl M. Weigert*

For the use of library visitors who wish to record quickly and cheaply small parts of articles or books for further study, three methods of making photographic copies are described. All have been tested over a considerable period of time and found to be practicable and valuable.

A commercially available reflex copying device, the Contoura†, consists of a portable light box used to press a sheet of sensitized paper into contact with an original by means of a plastic cushion. When used far enough away from incandescent room lighting or sunlit windows in the library, this method gives satisfactory results. Unfortunately many modern libraries have changed to fluorescent lights for illuminating the reading rooms and these produce enough ultraviolet to fog the reflex copying papers.

Fig. 1. Small, portable light source for exposing reflex prints, thin enough to be carried in a brief case. U. S. Patent Pending.

Looking around for a photographic copying paper that can withstand exposure to fluorescent light without fogging and still have a conveniently short exposure time under library conditions—up to half a minute—and at the same time not too expensive, the Kodak Autopositive paper was selected. This has been found useful in both the thin opaque and in the translucent form. The Autopositive emulsion is pre-solarized so that additional exposure to red or yellow light produces correspondingly lesser densities.

The need for a really small, portable light source for exposing the Kodak Autopositive paper has apparently not yet been met commercially so a working model was constructed that can be carried easily in a brief case. The device consists of tubular incandescent lamps arranged as shown in Figure one. So powerful is the light from this unit that exposure times on the order of 15 to 20 seconds (depending on the reflectivity of the original document) are the rule. The heat from 300 watts had to be dissipated by ventilation through the sides. Kodalith developer gave excellent contrast and several prints could be developed together to save time while using this otherwise slow-working developer.

Direct Reading Reflex Copies

Autopositive Translucent paper for copying material printed on both sides has been described in detail. First an intermediate, inverse reading, reflex copy is prepared from which a right reading final copy is then printed. Autopositive papers are considerably more expensive than negative papers and a shortcut (or one step method) was devised. There was no encouragement from the experts about a one step method but it was apparent from the beginning that there was a chance to obtain a right reading replica copy by exposing the emulsion side having it facing the light source with the back of the paper in contact with the print.

The first attempts were complete failures under any light conditions, and no contrast of any kind could be built up this way. The problem was finally satisfactorily solved by placing various kinds of sheet material in contact with the emulsion and in the path of the light. Only such materials that conveyed the light in a preferred orthogonal direction with very little light diffusing to the side were found to be useful. The effect that eliminates diffuse light and causes only the formation of coherent and perpendicular light rays could be called "Collimating" and the material suitable to produce such an effect appropriately: collimating material.

The simplest form of such material would be another autopositive sheet pressed with the emulsion side against the emulsion side of the copying sheet. Exposure times
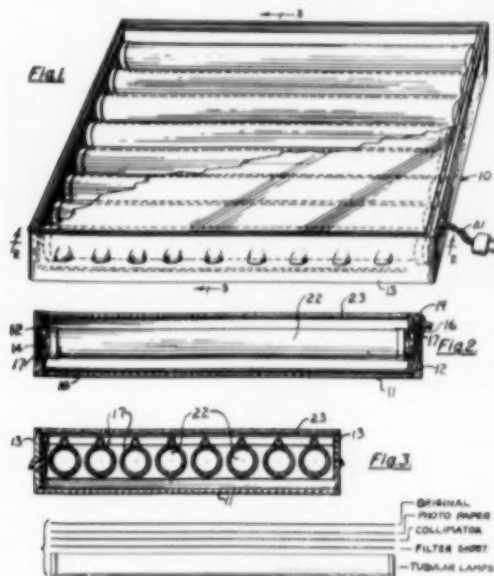
Fig. 2. Leica camera arrangement with auxiliary equipment for copying printed pages by existing light.

are rather prolonged and a frosted glass surface or a coating of similar kind to be found underneath most photocopying machines can be used. Although the dark parts lose considerably in density, enough contrast remains to make the copies easy to read. If the inverted print can be compared with the print of a book, copies made by the direct replica method would be similar to newsprint. It has been used for some time to record articles in magazines to file them in separate places.

Copying with the Leica

Another photocopying method was applied where only ordinary room light was available with the so-called "Leica Auxiliary Equipment." Ordinary Plus X Film was used with an opening of about f/6 to f/9 and about one-half second exposure. The reproduction from books was facilitated by pressing a glass plate on top covered by a frame of cardboard with holes to accommodate the legs of the stand. Cardboard flaps fastened to the frame marked the area covered by the exposure. Figure two gives a view of the simple easel and its construction. This device has been found useful in making diapositives in black on white from photocopy negatives or film negatives put on a light box, or even on a white background.

Experiments are under way also to reproduce color pictures from books and other colored surfaces.

Fig. 3. Simple equipment needed for reflex copying of book pages consists of two pieces of glass, a sheet of embossed cardboard for a pressure pad, a sheet of special negative paper, and a yellow filter.

A Simple Reflex Copying Method

Reflex copying of charts, diagrams, tables, or pages from books may be accomplished simply and without using special light boxes which have to be plugged into electrical outlets, sometimes in violation of library regulations.

Using Kodagraph Repro Negative paper, a "sandwich" consisting of a yellow acetate filter between two pieces of glass, and a piece of embossed, leather textured notebook cover paper, copies may be made using sunlight or bright sky illumination. The exposure varies from ten to twenty seconds, and usable reverse negatives, from which positives may be made later, can be produced with a minimum of disturbance in the library.

As shown in the attached photograph (Figure three), a piece of plain glass, or other rigid material is placed on a table, then the book, opened to the page to be copied is placed on the rigid backing. The leather textured paper, which has been found to promote good contact, is inserted under the page to be copied, a sheet of Repro
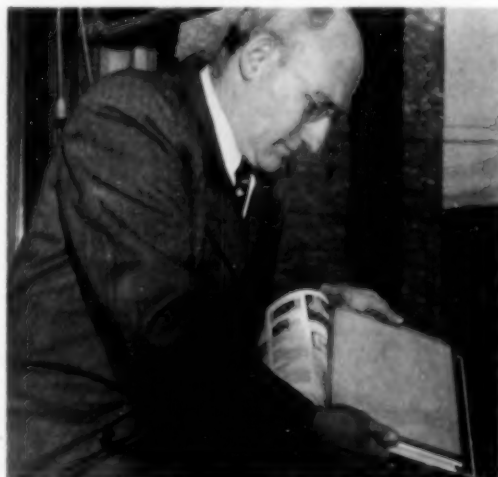
Fig. 4. The reflex copying "sandwich" shown in Figure three is exposed to sunlight or bright skylight at the nearest library window.

Negative paper is placed, emulsion side down, directly in contact with the material to be reproduced, and the whole is covered with the "sandwhich" of two pieces of glass with the yellow filter between them. The assembly is then taken to the nearest window (Figure four), and exposed for the required length of time. Contact between the sensitized paper and the material to be copied is assured by holding the ends of the assembly firmly in the hands during exposure.

A small quantity of developer carried in a dropper bottle will enable the copier to develop a small test strip to insure that the proper exposure is being used. Processing of the copies may be done at a later time.

Thanks is due to Mr. Vin Agar for taking the photographs for Figures three and four and to the librarians of the John Crerar Library for their permission to test the various methods on the spot.

DEPENDENCE OF THE RATE OF DEVELOPMENT OF SURFACE LATENT IMAGE ON THE TEMPERATURE OF THE DEVELOPER*

T. H. James

ABSTRACT

The purpose of the present work is to obtain information on the temperature dependence of development carried out under relatively simple conditions. Conclusions from such experiments can then be applied to the analysis of the behavior of more conventional developers. Most of the developers used in the present experiments are essentially of the type which develop only surface latent image. The photographic material was a simple motion-picture positive-type emulsion.

Amidol at pH 9.45 in the absence of added bromide develops the moderate- and high-exposure areas at a rate determined by the diffusion of the developer through the gelatin layer. The rate follows the Arrhenius equation, and the apparent activation energy is about 6.5 kcal/mole. In the areas of lower exposure, Amidol shows transition behavior. Diffusion is rate-controlling at high temperatures, but not at low.

Development by Metol at pH 8.5 follows the Arrhenius equation, and diffusion is not rate-controlling. The apparent activation energy increases with decreasing exposure. This change can be explained on the basis of the adsorption catalysis mechanism of development. Excess bromide in the developer accentuates the dependence of activation energy on exposure. At pH 9.5, diffusion becomes important in development of the high-exposure areas when the developer contains no bromide and the temperature exceeds 30–40 C. At pH 10.75, the rate of development by Metol is largely diffusion-controlled beyond the induction period over the entire temperature range in the shoulder region of the characteristic curve, but not in the toe region.

The dependence of activation energy on exposure influences the temperature dependence of the shape of the characteristic curve. Speed, measured as the reciprocal of the exposure to produce a density of 0.2 above fog, increases with increasing temperature for a fixed gamma. A rise in temperature increases the rate of development in the low-exposure regions relatively more than in the high-exposure regions, and the characteristic curve becomes flatter. The relative increase in fog is greater than that in image development. Hence, speed generally decreases somewhat with increasing temperature if development is carried to a fixed fog density.

THE RATE OF development of the latent image increases with increasing temperature of the developing solution. Several factors combine to determine the quantitative effect of temperature. Under certain conditions, one factor alone may dominate and mask the presence of the others, but under most experimental and practical conditions we must consider the possible contribution of the following factors to the over-all effect of temperature on development.

(1) An increase in temperature increases the specific rate of the chemical reaction or reactions involved. If a particular chemical reaction is rate-controlling, the temperature dependence over a limited range of temperature can be expressed adequately by the Arrhenius equation,

$$\text{Rate} = B \cdot \exp\left(-E/RT\right), \qquad (1)$$

where E is the activation energy, R is the gas constant, and T is the absolute temperature. B is substantially constant over a sufficiently limited range of temperature.

(2) At constant pH, the degree of ionization of the organic developing agents which contain hydroxyl groups increases with increasing temperature. If the ionized form is more active than the nonionized form, this means that the concentration of the more active form of the developing agent increases. Hence, the rate of development increases.

(3) The pH of a buffer solution of fixed composition generally *decreases* as the temperature increases. The change in pH depends upon the nature and composition of the buffer. The temperature dependence of development usually is determined at a fixed developer composition. Factors (2) and (3) thus act in opposite directions, but the effect of (2) usually exceeds that of (3).

(4) The rate of diffusion increases with increase in temperature. This factor is important whenever diffusion exerts a significant effect upon the over-all rate of development.

(5) The quantitative effect of temperature may depend upon the exposure of the photographic material. If so, this will influence the gamma–speed relation in its dependence on temperature. In general, fog formation is more dependent on temperature than is image development, and this too will be reflected in the dependence of the photographic characteristics of the developed material upon the temperature of development.

(6) The quantitative effect of temperature will depend upon the nature of the photographic material, the nature of the developing agent, and the composition of the developing solution.

Much of the literature on the temperature dependence of development deals with limited tests made with practical developer formulas, often under poorly controlled conditions. Such data are not suitable for theoretical analysis. Attempts to represent the temperature-dependence data mathematically have not been notably successful. Ferguson and Howard[1] suggested that the temperature coefficient of development of a particular photographic material in a particular developer is constant. If this suggestion were correct, a straight line

should be obtained by plotting the logarithm of the development rate against the temperature. Chibisoff and his associates[2] found that some developers followed this relation over a temperature range of 10–25 C, while others did not. They took as a measure of rate the time required to obtain a given gamma. Henn and Crabtree[3] found that the temperature coefficient of development was nearly constant over the temperature range of 60 to −10 F when they developed Kodak Super-XX Sheet Film in Kodak Developer SD-22 containing 50 percent glycol to prevent freezing. The assumption of a constant temperature coefficient, however, appears to be valid at best over only a limited temperature range for most developers, and the Arrhenius equation appears to fit the data equally well or better. The temperature coefficient derived from the Arrhenius equation varies only slightly with temperature over the range covered by most investigations of development. The Arrhenius equation itself gives a straight line when the logarithm of the rate is plotted against the reciprocal of the absolute temperature.

Fortmiller and James[4] found that the development of liquid emulsions by Metol (p-(methylamino)phenol sulfate), hydroquinone, and derivatives of p-phenylenediamine could be represented adequately by the Arrhenius equation. The same authors[5] found that the Arrhenius equation held for development of a coated motion-picture fine-grain positive film by vanadous ion, and James and Vanselow[6] found that the same equation held for development of that film by 1-phenyl-3-pyrazolidinone under some conditions. Uryu[7] found that the same relation held for development of a commercial emulsion by Metol under certain conditions, and Sugai and Furuichi[8] confirmed his findings with certain experimental emulsions. They also found that the activation energy calculated from the Arrhenius relation increased with increasing iodide content of the silver bromoiodide emulsions used.

The purpose of the present work was to obtain information on the temperature dependence of development carried out under relatively simple conditions where theoretical interpretation can be attempted. Conclusions from such experiments can then be applied to the analysis of the behavior of more conventional developers.

Experimental Materials and Procedure

The developers used in the present experiments are, with one exception, of the type which develop essentially only surface latent image. They are either free from sodium sulfite, or contain less than three grams of sulfite per liter. The use of such solutions avoids any complications which might arise from an effect of temperature upon the rate of solution of silver halide, physical development, or development of internal latent image. The photographic material used was a hardened fine-grain motion-picture positive film. This film can be processed over a relatively wide range of temperatures. The use of such a hard material tends to minimize the influence of temperature on the swelling of the gelatin layer, and hence to minimize any complication which could arise from this source.

All developers were prepared and used in an atmosphere of nitrogen. Agitation was supplied by irregular bursts of nitrogen passing through the solution. This method of agitation is a highly efficient one[9] and, moreover,
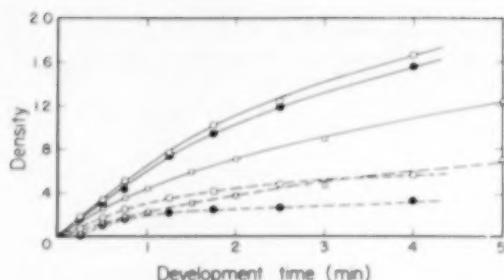

Fig. 1. Density–time of development curves. OO, Development by 0.00125 M Amidol at pH 9.45, no bromide; ●●, development by Amidol in the presence of 1 g. KBr/liter; □□, development by 0.00125 M 6-amino-3-diethylaminophenol at pH 10.0, no bromide. Solid curves represent log $E = 2.5$; broken curves, log $E = 0.6$.

supplies a safeguard against contamination of the developer solution by oxygen. The developer apparatus was jacketed, and the temperature was controlled to ± 0.2 C by water circulating through the jacket. The sensitometer strips were held by sulfur-free rubber bands to the outside of a hollow glass tube, and the tube was filled with water at the temperature of the thermostat.

The development runs were made at approximately 10-degree intervals over the temperature range of 10–60 C. The developer composition was kept constant for any set of experiments. The pH of the solution, therefore, varied with the temperature. The extent of this variation was determined, both experimentally and by reference to published tables on buffer compositions. The variation of development rate with pH at a fixed temperature was determined experimentally. These data were then used, when necessary, to calculate the development rates for a fixed pH at the various temperatures.

Borate buffers were used in all experiments in the pH range of 8–10. The effect of temperature on the pH of these buffers varied according to the composition of the buffer. A buffer composition containing 0.014 M borax and acid to give a pH of 8.50 at 20 C showed an almost constant decrement of 0.045 pH unit for each increase of 10 degrees in temperature. A similar buffer which gave a pH of 9.15 at 20 C showed a decrement of 0.07 pH unit, for an increase of 10 degrees, and a buffer which gave a pH of 9.50 showed a decrement of 0.09–0.10. Thus, the pH of a given borate solution decreases as the temperature increases. A carbonate-bicarbonate mixture was used to obtain a pH of 10.75 at 20 C. The temperature dependence of pH of this solution was not determined, since the variation of rate or development with pH was considered negligible for both p-(methylamino)phenol and 2,4-diaminophenol under the conditions used.

Development rates were measured in terms of the reciprocal of the time in minutes required to produce a density of 0.2 above base for log $E = 2.5$, and a density of 0.1 above fog plus base for log $E = 0.6$. It seemed incorrect to apply a fog correction for the development of the high-exposure image, since practically all of the grains are made developable by this exposure. However, it was found that even if a "correction" was made by subtracting fog from image densities at this high exposure, no significant change occurred in the results for any except

the highly fogging 2,4-diaminophenol because the fog was negligible in most instances when the image density was only 0.2. Even with the 2,4-diaminophenol developers, the fog density was significant only at the higher temperatures. Development rates also were measured in terms of the maximum slope of the density–time of development curve for $\log E = 2.5$, and the average slope in the density interval 0.2–0.4 for $\log E = 0.6$. The fog rates were measured in terms of the reciprocal of the time required to give a fog density of 0.1. Photographic speed was measured in terms of the reciprocal of the exposure required to give a density of 0.2 above fog plus base. All exposures were made on the Eastman IIb Positive Sensitometer, and densities were read on a recording physical densitometer.

Development by Amidol (2,4-diaminophenol dihydrochloride)

Some preliminary tests were made on the pH-dependence of development by Amidol. The concentration of developing agent was 0.00125 M, and the solution contained neither sulfite nor bromide. Development by Amidol showed little or no induction period. The rate increased with increasing pH up to a pH of about 9. The rate showed only slight dependence upon pH in the region 9.0–10.8, and decreased at higher pH. Data are give in Table I.

Table I

DEVELOPMENT BY AMIDOL

pH	Log E = 2.8 1/t (D = 0.2)	Log E = 0.9 1/t (D = 0.1)	Log E = 0.4 1/t (D = 0.1)	Fog 1/t (D = 0.1)
8.0	2.0	1.7	1.4	...
9.0	3.6	3.8	2.3	0.08
9.7	3.6	3.8	2.5	.15
10.8	3.0	4.0	2.6	.42
12.6	1.4	1.4	0.8	.53

The rate of image development by Amidol at pH above 9 and in the absence of added bromide is largely or entirely diffusion-controlled. This is proved by the following experimental observations:

(1) Cross sections of the image in the high-exposure areas were obtained for various stages of development. Examination of these cross sections under the microscope showed that practically all of the grains in the surface layer of the emulsion develop first, then development progresses into the depths of the emulsion. The density of the developed image is approximately proportional to the thickness of the developed layer when the exposure is sufficient to make practically all of the grains developable.

(2) The preceding microscopic investigation is supported by visual observation of the developing strips under a Kodak Wratten No. 0 Safelight Filter. After development for a minute or two in the 0.00125 M Amidol solution, the sensitometric image appeared to be quite strong when viewed from the emulsion side, but was scarcely visible when viewed from the base side. As development progressed, the image became readily visible from the base side, but the high-exposure end appeared to be surrounded by a line of much greater density. Mi-
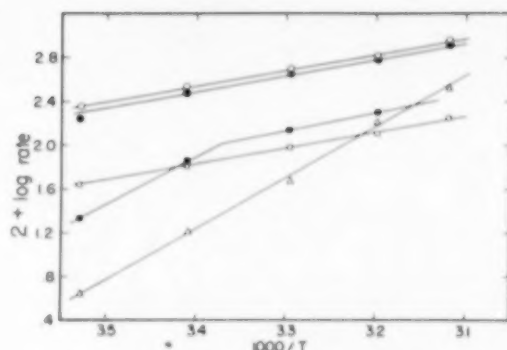
Fig. 2. Arrhenius plots for Amidol developer at pH 9.45. ○○, 1/t rates, log $E = 2.5$; □□, slope rates, log $E = 2.5$; ●●, 1/t rates, log $E = 0.6$; ■■, 1/t rates, log $E = 0.0$; △△, 1/t rates for fog.

crodensitometer traces showed that this line was indeed denser on the fixed-out emulsion, but only by about 10 percent. This line evidently is the result of an edge effect caused by diffusion of developer from the unexposed area into the exposed area.

(3) The rate of development by Amidol in the pH region 9–11 is somewhat greater than the rate of development by 6-amino-3-diethylaminophenol at pH 10.0. The rate of development of coated film by the latter compound is known to be diffusion-controlled, since the rate of development of the corresponding liquid emulsion by this agent is at least 60 times that of the coated emulsion.[4] The fact that the rate of development of the coated emulsion by Amidol is somewhat greater than the rate of development by 6-amino-3-diethylaminophenol instead of exactly equal to it is to be expected, since the Amidol molecule is smaller and spatially more compact.

Figure one shows a comparison of the density–time of development curves for Amidol at pH 9.45 and 6-amino-3-diethylaminophenol at pH 10.0. The rate of development by the bromide-free Amidol is greater than that by the 6-amino-3-diethylaminophenol throughout the entire course of development for $\log E = 2.5$. The rate of development by Amidol likewise is greater in the early stages for $\log E = 0.6$, but development by 6-amino-3-diethylaminophenol eventually overtakes it. The addition of 1.0 gram of potassium bromide per liter of Amidol developer decreases the rate of development in the high-exposure area only slightly. Diffusion still is largely rate-controlling even in the presence of the bromide for the heavily exposed film. The rate of development in the lower-exposure area, however, is only about one-half as great as it is in the absence of bromide, and some other rate process must be playing a part in determining the over-all rate.

The preceding experimental observations establish that the rate of development by the bromide-free Amidol, at least in the high-exposure areas, is determined by the rate of diffusion of the developer through the gelatin layer of the hard film used. This developer, accordingly, is well suited to a study of the effect of temperature on development in a diffusion-controlled system. A 0.00125 M solution of Amidol in a borate buffer was used for this purpose. Figure two shows the temperature-dependence
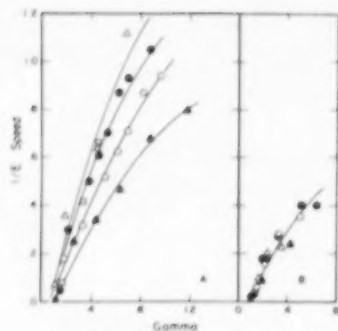
83

Fig. 3. Gamma–speed plots. A. Amidol developer.
▲▲, 10.3 C; ○○, 20.2 C; ●●, 30.4 C; △△, 39.8 C; □□,
47.8 C. B. 1-Phenyl-3-pyrazolidinone developer.
▲▲, 4.9 C; ○○, 20.2 C; ●●, 29.7 C; △△, 40.2 C.

relations. The $1/t$ and maximum slope rates are well
represented by the Arrhenius equation over the entire
temperature range for the high exposures as shown by the
straight lines obtained in the logarithm rate $vs.$ $1000/T$
plots. The activation energy is 6.4–6.6 kcal/mole, which
is identical with that found by Fortmiller and James[8] for
diffusion-controlled development by vanadous ion, and
is within the range of 5.3–8.3 kcal/mole found by Lu-
Valle, Dunnington, and Margnetti[10] in their study of the
diffusion of hydroquinone in gelatin layers. The $1/t$
rates for log $E = 0.6$ fall on a straight line of the same
slope as that formed by the rates for log $E = 2.5$ for tem-
peratures of 20–50 C, but the point corresponding to the 10
C temperature falls slightly below this line.

A greater divergence is observed in the points repre-
senting the $1/t$ rates for log $E = 0.0$ at both 10 and 20 C.
This behavior suggests that, at these low temperatures,
diffusion is no longer entirely rate-controlling in the
development of the low-exposure areas. This deduction
is supported by a comparison of the development curves
for Amidol and 6-amino-3-diethylaminophenol. Data
for the latter compound are not available at 10 C, but the
curves given in Figure one for 20 C show that, although
Amidol is faster in the early stages of development of the
log $E = 0.6$ area, the curves cross and the 6-amino-3-
diethylaminophenol becomes faster above a density of
0.5. At log $E = 0.0$ (not shown), the two agents start
to develop at the same rate, but the Amidol is definitely
slower above a density of about 0.15. We may conclude,
therefore, that the rate of development by Amidol in the
low-exposure region is not entirely controlled by diffu-
sion at 20 C, and that the break in the log rate $vs.$ $1/T$
plot representing log $E = 0.0$ in Figure two represents a
transition away from the state of complete diffusion con-
trol. We shall encounter other examples of this behavior
subsequently.

The rate of fog formation is not controlled by the rate
of diffusion of the developer through the gelatin layer.
If it were, the grains in the unexposed areas would be
reduced as fast as those in the exposed areas. The over-
all activation energy of fog-density formation, as derived
from Figure two, is about 21 kcal/mole, and probably
represents a chemical step in the formation of fog centers
in the silver halide grains. The net rate of development
of fog density is controlled by the rate of formation of
fog nuclei which can initiate the catalyzed reduction of
the grains. Such nuclei probably are formed by reduction
of silver ions on the grain surface, perhaps at dislocations
or adjacent to silver sulfide molecules.

If diffusion were rate-controlling at all temperatures,
even at the exposure threshold, we should expect that the
gamma–speed relationship would be essentially independ-
ent of temperature, providing the fog level is too low to
influence the gamma seriously. As we have seen, how-
ever, diffusion is not entirely rate-controlling at low
exposures and low temperatures for the Amidol de-
veloper, and this is reflected in the speed–gamma relation
shown in Figure three. Speed increases with increasing
temperature over the range 10–30 C when gamma is held
constant. There is little dependence of speed on tempera-
ture above 30 C.

The rate of development by 1-phenyl-3-pyrazolidinone[*]
at pH 13 appears to be diffusion-controlled even in the
toe region of the characteristic curve and over the entire
range of temperatures investigated (5–40 C). The right-
hand portion of Figure three gives the speed–gamma rela-
tion for this developer. Speed obtained for a given gam-
ma is essentially independent of temperature, as expected.
Development was restricted to relatively low gamma
values because of the marked fogging tendency of this
developer.

Development by Metol and Metol–Ascorbic Acid Mixtures

Metol should diffuse through a gelatin layer about as
rapidly as Amidol. Accordingly, if development by
Metol under a particular set of conditions is much slower
than development by an equal molecular concentration
of Amidol at pH 9.45, we may conclude that diffusion of
the Metol through the gelatin layer is not rate-control-
ling. This is the situation when Metol is used at pH
8.5. It may be suggested that since ionized p-(methyl-
amino)phenol is more active than the nonionized form,
the concentration of the ion should equal the molecular
concentration of Amidol in making the rate comparison.
If this is done, the rate of development by Metol appears
to be greater than that by Amidol by over an order of
magnitude. Such a comparison, however, is not valid,
since the rate of ionization of the developing agent is
undoubtedly much greater than the rate of diffusion,
and hence, diffusion of the nonionized form is contribut-
ing to the concentration of ionized developing agent
within the gelatin layer.

There is other evidence to show that diffusion of the
developer through the gelatin layer is not rate-control-
ling when Metol is used at pH 8.5. Visual examination
of the developing strips shows that the image appears
almost as soon in the high-exposure areas when the film
is viewed from the base side as when it is viewed from the
emulsion side. Microscopic examination of cross sections
of the film show that developed silver appears through-
out the thickness of the emulsion layer even at quite
low developed densities (Figure four A), and the size of
the developed particles throughout the layer is much
smaller than the size of the silver halide grains.

Metol–Ascorbic Acid Development at pH 8.5

The developer used in this part of the work consisted of 0.278 gram of Metol and 2.78 grams of 1-ascorbic acid per liter, and 0.014 M borax as buffer. The ascorbic acid at this pH acts only to prevent the accumulation of oxidized Metol, and the developer is effective only for surface latent image. The developer shows a marked induction period. The $1/t$ rates of development increased with pH as about the 0.4 power of the hydroxyl-ion concentration in the pH range 8.2 to 8.8. The slope rates varied as approximately the same power. This dependence on fractional power can be accounted for on the basis of adsorption of the ionized form of the developing agent. Levenson[11] has shown that the rate of development by Metol varies as a fractional power of the concentration of the developing agent at a fixed pH, and that the fractional power is increased by the addition of bromide.
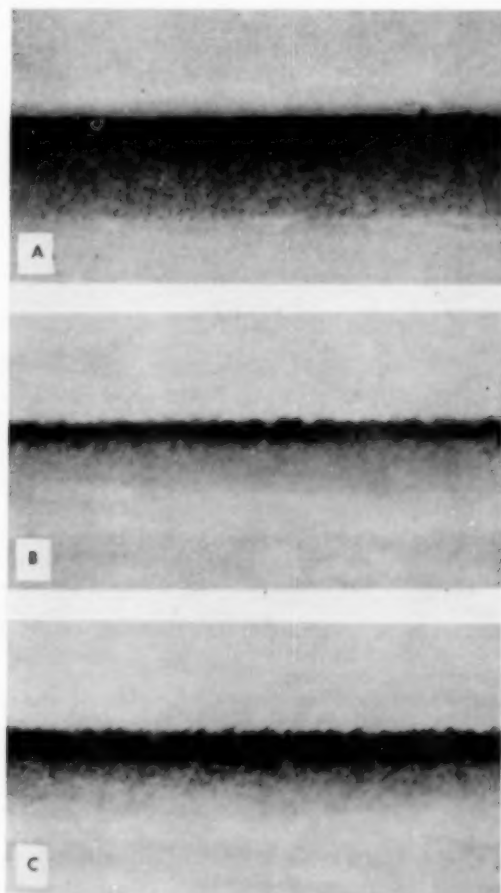
Fig. 5. Arrhenius plots for Metol–ascorbic acid developer at pH 8.5. OO, $1/t$ rates, log $E = 2.5$; □□, slope rates, log $E = 2.5$; ●●, $1/t$ rates, log $E = 0.6$; ■■, slope rates, log $E = 0.6$; △△, fog rates.

Increase in pH effectively increases the concentration of the active developing agent.

Figure five shows the Arrhenius plot of log rate against the reciprocal of the absolute temperature. A straight line is obtained for each of the various expressions of rate employed. The activation energies obtained, however, depend upon the method of expressing the rate (see Table II). To clarify this point, we must consider the meaning of each method of expressing rate in terms of the development of the individual grains of the emulsion.

Table II

OVER-ALL ACTIVATION ENERGIES CALCULATED FOR VARIOUS METOL DEVELOPERS

Developer	KBr g/l	pH	Log $E = 2.5$ $1/t$	Slope	Log $E = 0.6$ $1/t$	Slope	Fog $1/t$
Metol-Ascorbate	0	8.5	14.0	12.9	15.6	...	...
Metol-Ascorbate	1	8.5	20.9	16.1	23.7	28.5	30
Metol-Ascorbate	5	8.5	20.7	17.7	23.7	29.2	32
Metol-Ascorbate-Sulfite ‡	0	8.5	15.4	13.1	16.6	14.0	22
Metol	0	9.5	12.9	10.1	13.7	17	27
Metol-Sulfite	0	9.5	12.9	10.1	13.7	17	23
Metol-Ascorbate	0	9.7	13.8	10.1	15.0	18.4	28
Metol-Sulfite	0	10.75	8.7	7.1*	10.1	12.2	21
Metol-Sulfite	1	10.75	10.8	7.1*	14.0	24	...
Metol-Sulfite	5	10.75	15.2	11.7†	25	...	...
Metol-Sulfite	10	10.75	15.2	12.0†	26	...	...

* Diffusion control.

† Low temperature range.

‡ At log $E = 0$, the activation energy for the $1/t$ rates is 17.2; that for the average slope rates between $D = 0.1$ and 0.2 is 19.6.

Fig. 4. Photomicrographs of cross sections of developed images. Magnification, 2,500X. A. Development by Metol–ascorbic acid–KBr solution at pH 8.5 to density 0.57. B. Development by Metol–sulfite developer at pH 10.75 to density 0.36. C. Same developer as B, but development to density 0.81. All exposures to log $E = 2.5$.
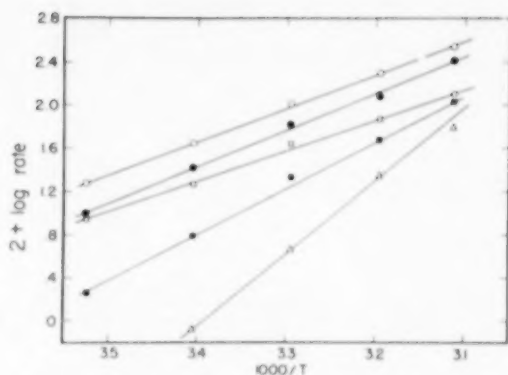
The $1/t$ rates are primarily induction-period rates for this developer. The maximum slope rates for development of the high-exposure sensitometer steps are essentially rates of development of the grains beyond the induction period. This has been demonstrated previously[12] for two similar motion-picture positive materials by three methods: measurement of variation of covering power with duration of development, measurement of relative bromide-ion sensitivity at various stages of development, and actual microscopic examination of the grains at vari-
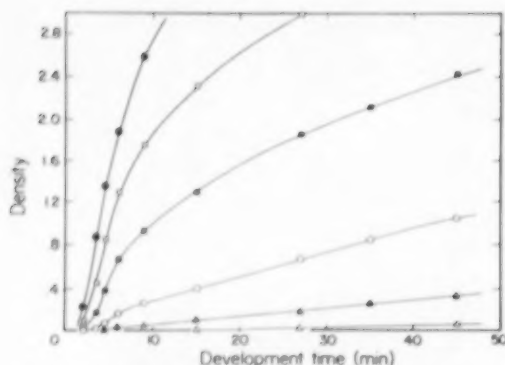
Fig. 6. Density–time of development curves for Metol–ascorbic acid–KBr developer at pH 8.5 and 40.2 C. Log E values: ●●, 2.5; □□, 1.6; ■■, 1.1; ○○, 0.6; ▲▲, 0.2; △△, fog.

ous stages of development. It was confirmed with the present emulsion by observations on the change in color of the image and by actual microscopic inspection of the silver deposits. A red to red-brown image is obtained in the early stages of development of the high-exposure areas. The color changes as development progresses and becomes black at fuller development.

A different situation exists for development in the toe region of the characteristic curve. This image is black even at relatively low densities, and the image grains appear to be nearly all fully developed. Of course, a considerably longer development time is required to bring up the image in this region than in the high-exposure region. In this low-exposure region, the induction periods of the individual grains vary considerably, and the increase in density with increased development is caused primarily by an increase in the number of developed grains. In this exposure region, therefore, even the slope rates must be considered as essentially induction-period rates. An average slope measured between a density of 0.3 and 0.5 for log $E = 0.6$ represents the induction period of a class of grains which have longer induction periods than those represented by the $1/t$ rates for density $= 0.1$.

The shape of the density–time of development curves varies with the exposure, and the change is a consequence of the transition from the one extreme mode of development to the other. Figure six shows the family of curves obtained with a Metol–ascorbic acid developer containing 1 gram of potassium bromide per liter. The curve for log $E = 0.6$ shows a break at a density of about 0.2, and the curve beyond this point is nearly straight up to a density of about 1.0. The curve for log $E = 0.2$ is straight almost from its inception and over the same range of development time.

The over-all activation energies for the various Metol–ascorbic acid developers are recorded in Table II. No attempt has been made to correct these values either for the heat of ionization of p-(methylamino)phenol or for the heat of adsorption. The latter is completely unknown. The former has not been determined directly for p-(methylamino)phenol, but it is known for hydroquinone, and it is unlikely that the values for the ionization of the hydroxyl groups in these two compounds dif-

fer by more than 1–2 kcal/mole. If this is so, the correction for ionization would decrease the activation energies given by approximately 2 to 3 kcal/mole. Essentially the same correction would be applied to all of the values given for the bromide-free developer.

An examination of the values given in Table II shows that the induction-period activation energy increases with decreasing exposure. The energies calculated from the $1/t$ rates for the bromide-free developer show an increase of 1.6 kcal/mole in going from an exposure of log $E = 2.5$ to log $E = 0.6$. This value is well beyond the limits of experimental error. The difference between the energy calculated from the $1/t$ rates and the slope rates for log $E = 0.6$ is even greater, and this indicates a considerable difference in reactivity among the grains in this one exposure step. The maximum slope rates for the log $E = 2.5$ step give an activation energy somewhat smaller than that applying to the induction-period region.
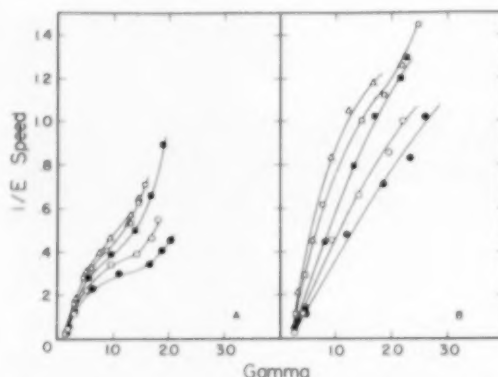

Fig. 7. Gamma–speed plots for Metol–ascorbic acid developers at pH 8.5. A. No sulfite. ●●, 10.7 C; ○○, 20.6 C; ■■, 30.5 C; □□, 39.9 C; △△, 48.2 C. B. Sulfite present. ●●, 10.5 C; ○○, 19.8 C; ■■, 30.4 C; □□, 39.7 C; △△, 47.7 C.

The activation energies calculated for development by p-(methylamino)phenol at pH 8.5 are much higher than the 6–7 kcal/mole expected for a diffusion-controlled process. On the other hand, they agree with the value of 16 kcal/mole obtained by Fortmiller and James[6] for the development of the liquid emulsion where only a single exposure level was used.

Excess bromide ion in the developer decreases the rate of development and increases the dependence of rate upon both pH and temperature. A developer of the same composition as the preceding, but containing 1.00 gram of potassium bromide per liter, showed a dependence of rate upon the 0.8–0.9 power of the hydroxyl-ion concentration over the pH range 8.2–8.8. Once more, the rate-temperature relation is adequately expressed by the Arrhenius equation. The bromide-ion addition accentuates the differences in activation energies obtained under the different exposure conditions (Table II). When the bromide concentration is increased to 5 grams per liter, the rates of image development and fog formation are decreased further, but little or no further change occurs in the calculated activation energies.

More information on the detailed mechanism is needed before the temperature-dependence data on fog formation by the Metol–ascorbic acid developers can be accurately assessed. The fog silver formed in the absence of added potassium bromide is highly colored (yellow to red) to transmitted light. The fog areas contain some particles of about the same size as the original silver halide grains, but they also contain a considerable amount of much more finely divided silver. The growth of the finely divided particles may occur primarily by physical development. On the other hand, the fog formed in the presence of 5 grams of potassium bromide per liter is nearly black to transmitted light, and consists primarily of silver grains of about the same size as the original halide grains. The fog formed by a developer to which sulfite has been added but not bromide is more nearly spectrally neutral than that formed by the sulfite-free developer, but still shows some color. The fog silver formed by the Amidol developer is of substantially the same particle size and neutral tone as the image silver.

A further point to remember in considering the present data is that even the developers to which no bromide had been added initially contain some bromide during much of the course of fog formation. This added bromide may increase the temperature-dependence of fog formation by such solutions. It will not be of significance when the Metol–ascorbic acid solutions of pH 8.5 contain 1 to 5 grams of potassium bromide originally.

The temperature-dependence data for the Metol–ascorbic acid developer without bromide, but now containing 27.8 grams of sodium sulfite per liter, likewise fit the Arrhenius equation. The sulfite exerts a definite solvent action on the silver halide at this concentration. The sulfite causes a slight increase in the activation energies for the $1/t$ rates at both exposure levels, but causes a significant drop in the value calculated from the average slope rates at $\log E = 0.6$. The sulfite also produces a significant drop in the activation energy for fog formation. This latter result is in keeping with the enhanced fogging activity of the developer containing sulfite, and is probably dependent on the solvent action of the sulfite on silver bromide. Such solvent action may reveal sur-
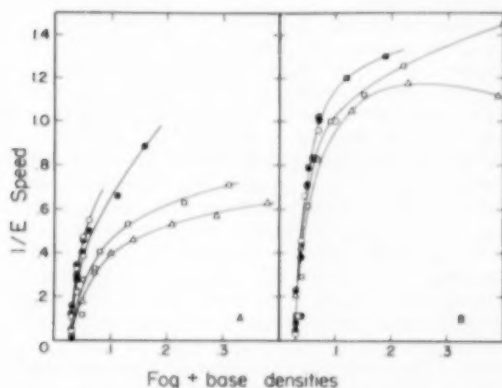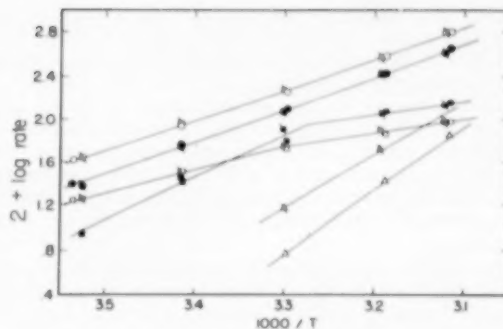

Fig. 9. Arrhenius plots of Metol developers at pH 9.5. ○○, $1/t$ rates, $\log E = 2.5$; □□, slope rates, $\log E = 2.5$; ●●, $1/t$ rates, $\log E = 0.6$; ■■, slope rates, $\log E = 0.6$; △△, fog rates. Points marked with a cross line represent the same developer with the addition of 1.4 g sodium sulfite per liter.

face which is more susceptible to fogging attack by the developer, or may promote reaction between developer and silver ions in solution by supplying the silver ions at a higher rate than water alone can. At least part of the fog shows characteristics of "physical" development.

Figure seven illustrates the dependence of the gamma–speed relation upon the temperature in the presence and in the absence of sulfite. In general, the photographic speed obtained at a fixed gamma increases with increasing temperature, but the shapes of the speed–gamma curves vary with the composition of the developer. Sulfite, which lowers the activation energy in the low-exposure region, increases the photographic speed for a given gamma. On the other hand, the fog obtained by development to a fixed gamma increases with increasing temperature, and the fog obtained by development to a fixed speed increases with increasing temperature. The fog–speed relationships are shown in Figure eight.

Development by Metol at pH 9.5

Development by Metol (0.00125 M) at pH 9.5 shows a definite induction period. The induction-period rates follow the Arrhenius equation over the entire temperature range, as shown in Figure nine. The activation energies are only slightly lower than those found for the Metol–ascorbic acid developer at pH 8.5. The difference, if real, may be attributed to the higher degree of ionization of the p-(methylamino)phenol at pH 9.5. There is no evidence of diffusion control in the induction-period region.

The maximum slope rates for the high exposure and the average slope rates for the low exposure exhibit transition behavior as the temperature is increased. A break occurs in the curves in the region of 30–40 C. The slope prior to the break corresponds to a somewhat smaller activation energy than found at pH 8.5. The slope beyond the break corresponds to an activation energy of 6–6.5 kcal/mole, which is substantially that found for the diffusion-controlled development by Amidol.

The addition of 1.4 grams of sodium sulfite per liter of Metol developer has no significant effect upon the rate of development at pH 9.5. As shown in Figure nine, the

Fig. 8. Fog-speed plots for Metol–ascorbic acid developers at pH 8.5. A. No sulfite. ●●, 10.7 C; ○○, 20.6 C; ■■, 30.5 C; □□, 39.9 C; △△, 48.2 C. B. Sulfite present. ●●, 10.5 C; ○○, 19.8 C; ■■, 30.4 C; □□, 39.7 C; △△, 47.7 C.

rates for the sulfite-containing developer fall upon the same lines as the corresponding points for the sulfite-free developer. The sulfite increases the rate of fog formation, however, and decreases the activation energy of fog formation. A similar effect of sulfite upon fog was observed at pH 8.5, where the concentration of sulfite was 20 times as great as in the present experiments. Evidently, the solvent action of the relatively low sulfite concentration used here is not enough to influence image development, but does influence the slower process of fog formation.

The speed–gamma curves for this developer are given in the left half of Figure ten. The curves resemble in shape those obtained with the Metol–ascorbic acid developer at pH 8.5.

Development by Metol–Ascorbic Acid at pH 9.7

The Metol–ascorbic acid combination used at pH 9.7 contained 0.00125 M Metol, and 0.008 M l-ascorbic acid, and no bromide. This developer gave results which are strikingly similar to those obtained at pH 8.5 (see Table II). The induction period activation energies are substantially the same as those observed at the lower pH; the activation energy beyond the induction period is somewhat lower. The shapes of the gamma–speed curves likewise are similar.

There is no evidence that diffusion controls development rates below 40 C. Some transition may occur between 40 and 50 C, but this is not certain. This difference in behavior between the Metol–ascorbic acid developer and the Metol or Metol–sulfite developer probably lies in the role played by the ascorbic acid. In the former developers, p-(methylamino)phenol is oxidized during development, and can only be replaced by diffusion of fresh p-(methylamino)phenol from the solution. In the latter, ascorbic acid is present in considerable excess and acts to regenerate the p-(methylamino)phenol. Oxidized Metol thus need not be replaced by diffusion from the solution so long as a sufficient supply of ascorbic acid is present in the vicinity of the development reaction.

Development by Metol at pH 10.75

The temperature dependence of development by Metol was determined at pH 10.75. The solution contained 0.00125 M Metol and 0.022 M sodium sulfite, and was buffered to pH 10.75 at 20 C with a carbonate–bicarbonate solution. The change in pH of this buffer with change in temperature was not determined, since the rate of development by Metol is relatively insensitive to pH in this region. Approximately three-fourths of the p-(methylamino)phenol is ionized at pH 10.75 and 20 C, and any correction for change in pH with temperature would change the calculated activation energies by less than 1 kcal/mole.

Metol at this pH develops with a small induction period, and the induction-period rates follow the Arrhenius equation over the temperature range studied (10–40 C). The data are given in Table II. The activation energies calculated for the induction period at each exposure level are about 4 kcal/mole less than those calculated for pH 9.5. The difference may be accounted for largely on the basis of the heat of ionization of the
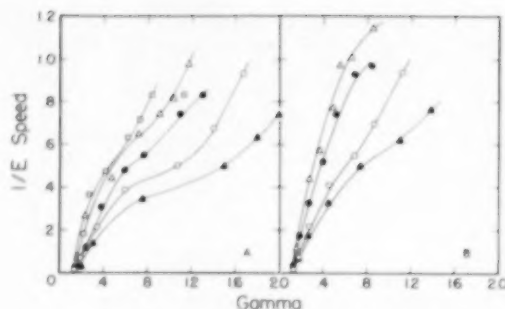

Fig. 10. Gamma–speed plots for Metol–sulfite developers. A. pH 9.5 ▲▲, 10.6 C; ○○, 19.8 C; ●●, 30.0 C; △△, 40.2 C; □□, 47.6 C. B. pH 10.75. ▲▲, 10.1 C; ○○, 20.4 C; ●●, 30.4 C; △△, 40.8 C.

p-(methylamino)phenol, if that heat is assumed to be the same as for the ionization of a hydroxyl group of hydroquinone (about 5 kcal/mole).

The maximum slope rates for the high-exposure level likewise follow the Arrhenius equation. The calculated activation energy, however, is about that to be expected for a diffusion-controlled process at this pH. The curve representing the average slope rates at the low-exposure level is much steeper in the lower temperature region, but breaks at about 30 C, and the last portion of it has the slope expected for a diffusion-controlled process.

Addition of 1 gram of potassium bromide per liter to the developer increases the relative induction period, and also increases the calculated activation energy. The activation energies are about 10 kcal/mole lower than those obtained with the Metol–ascorbic acid developer at pH 8.5 in the presence of bromide. An increase in bromide to 5 grams per liter increases the calculated activation energy, but no further change occurs when the bromide is increased to 10 grams per liter. The Arrhenius curves are shown in Figure eleven. The higher the temperature, the smaller is the retarding action of bromide on development.

The calculated activation energy for development of the high-exposure step beyond the induction period is the same in the presence of 1 gram of potassium bromide as in its absence. All evidence points to diffusion as the controlling factor in the rate of development in this region. The appearance of the developing strips, when viewed through the base, is the same as that of the strips developed in Amidol. Cross sections cut from the film in various stages of development and examined under the microscope show clearly that development takes place rather fully in the upper portion of the emulsion layer before any significant amount occurs in the depths, and that development then progresses by penetrating deeper into the emulsion layer (cf. Figure four B, C). The distribution of developed image parallels that observed with the diffusion-controlled Amidol developer. Finally, a comparison of the rates of development by Amidol and Metol shows that the two are nearly equal *beyond the induction period*. This is illustrated in Figure twelve, which also contains the curves for development at pH 9.5. These curves further illustrate the fact that development by Amidol is slower at pH 10.8 than it is at pH 9.5.

The rate of development by the Metol solution containing 1 gram of potassium bromide at pH 10.75 is slower in the toe region of the characteristic curve than is the rate of development by Amidol, and the activation energy of development by Metol is considerably greater than that of diffusion. Diffusion, therefore, is a factor of major importance in determining the rate of development of the high-exposure areas, but is of little or no significance in determining the rate of development of the low-exposure areas.

The speed–gamma curves for the Metol–sulfite developer at pH 10.75 are given in the right half of Figure ten. The S-shaped curve which characterized the relation at pH 9.5 is largely or wholly absent at pH 10.75.

Discussion and Conclusions

The present investigation has shown that the temperature dependence of development of a hard motion-picture positive emulsion is well represented by the Arrhenius equation under conditions such that only surface latent
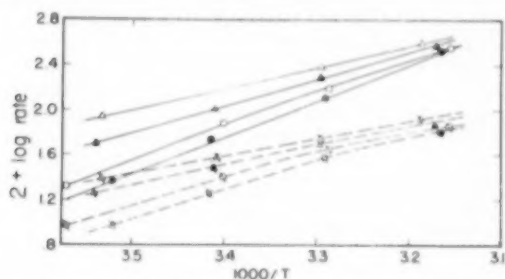

Fig. 11. Arrhenius plots for Metol–sulfite developer at pH 10.75 and log E = 2.5. $\triangle\triangle$, No KBr; $\blacktriangle\blacktriangle$, 1 g KBr/l; OO, 5 g KBr/l; $\bullet\bullet$, 10 g KBr/l. Solid curves represent $1/t$ rates; broken curves, slope rates.

image is involved and diffusion is rapid compared with the chemical reaction. If diffusion is rate-controlling, the temperature dependence once more is represented by the Arrhenius equation, and the activation energy indicated is that of the diffusion process. Intermediate conditions can be recognized by a transition as temperature increases in the indicated activation energy from that representing the chemical reaction to that representing the diffusion process. Diffusion plays no significant part in determining the rate of development by Metol at pH 8.5. At pH 9.5, diffusion becomes important in the high-exposure areas when the temperature exceeds 30–40 C and the developer contains no bromide. At this pH, development by Amidol in the absence of added bromide is diffusion-controlled over most of the exposure range represented by the characteristic curve. At pH 10.75, the rate of development by Metol is diffusion-controlled beyond the induction period in the higher-exposure areas, but not in the toe region of the characteristic curve.

This investigation has also shown that the over-all activation energy of development by Metol is dependent upon the amount of exposure when diffusion is not rate-controlling. As the exposure increases, the activation energy decreases. This dependence of activation energy upon exposure becomes more pronounced when bromide is present in the developer.
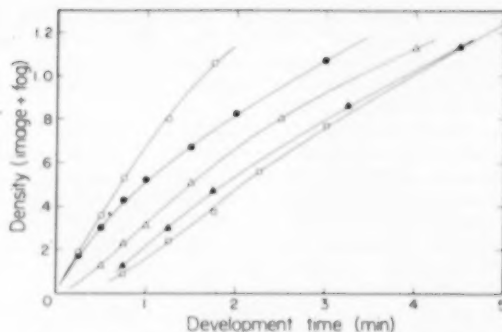

Fig. 12. Density–time of development curves for log E = 2.5 and 20 C. OO, Amidol, pH 9.5; $\bullet\bullet$, Amidol, pH 10.8; $\triangle\triangle$, Metol, pH 10.75; $\blacktriangle\blacktriangle$, Metol–KBr, pH 10.75; $\square\square$, Metol, pH 9.5.

The over-all activation energy, as calculated from the Arrhenius equation, is a composite value which may include terms representing the heat of ionization of the developer, the heats or activation energies of adsorption of the developer and desorption of the oxidation products, as well as the activation energy of the actual chemical change. The over-all activation energy can be corrected for the heat of ionization if the heat of dissociation, the dependence of rate upon the concentration of the developer ion, and the degree of ionization at a particular temperature and pH of the developer are known. The correction applied actually represents a correction for the change in concentration of the active developer species with change in temperature. Since the development rate is more dependent upon the developer-ion concentration when bromide is present, the correction applied to the data in Table II will be greater for the developers containing bromide than for the others. At pH 8.5, however, the difference will account for an increase of only 2 to 3 kcal/mole produced in the over-all activation energy by the addition of bromide. The observed increase produced by 5 grams of potassium bromide per liter varies from 5 to 10 kcal/mole, depending upon the exposure and the particular development rate considered.

The additional increase over that attributable to the heat of dissociation may represent an actual increase in the activation energy of the chemical reaction. Increased bromide-ion concentration should decrease the activity of the surface silver ions because of the electrostatic attraction between the two ion species. The increase also may represent a change in the adsorption factor. No data are available from which heats of adsorption of the developer can be calculated, but there is evidence of competition between bromide ion and developer for adsorption sites, and this may be reflected in the heats of adsorption. There is no reason to suppose that the heat of adsorption of either is independent of the amount of surface coverage.

At a pH of 10.75, the increase in over-all activation energy caused by the addition of 1 gram of potassium bromide per liter is much smaller than at pH 8.5. The maximum change at pH 10.75 is not reached until about 5 grams of potassium bromide per liter have been added, whereas the maximum has been reached at 1 gram at pH 8.5. This difference may arise from failure to establish

adsorption equilibrium at the lower concentration of bromide when the pH is 10.75. The rate of the development reaction is considerably greater at this pH than at pH 8.5, and a higher concentration of bromide may be needed for this reason alone.

The observed dependence of activation energy on exposure is in accord with the view that development depends upon adsorption catalysis. The fundamental basis for photographic development is the enhanced reactivity of silver ions in the presence of silver nuclei. Silver ions are reduced to metallic silver by electrons derived from the developing agent. The rate of this reduction is greater when the silver ions are in contact with metallic silver nuclei, and hence more silver is deposited in the presence of such nuclei than in their absence. Adsorption of silver ions by the catalyzing nuclei is the factor of major importance in promoting the reaction.[12] It permits the reaction to proceed with a smaller activation energy than that required for reaction of a silver ion in solution or on the surface of pure silver halide. In physical development, the silver ion is adsorbed from solution prior to reaction. In direct chemical development, the silver–silver halide interface is the favored spot for reaction. The silver ions at this interface are already subjected to adsorption forces and are probably displaced from their normal lattice positions.

The adsorption forces at the silver–silver halide interface should depend, to some extent, upon the size and configuration of the latent-image nucleus, and this, in turn, depends upon the exposure. The activation energy, as a consequence, may vary with exposure. If the developer is adsorbed and forms a complex with silver ion prior to reduction of that ion, as suggested by a considerable body of evidence,[14] reaction occurs at a triple interface between silver, silver halide, and developer. The dependence of activation energy on exposure could then vary with the developing agent.

The temperature dependence of the solvent action of water or other solvent on silver bromide could influence the calculated activation energies under certain conditions. If, for example, some of the latent-image centers in the lower-exposure region did not become effective in promoting development until a localized solution of some silver halide made them accessible to the developer, the rate of development would depend upon the rate of such solvent action. The rate of solvent action should increase with increase in temperature, but the quantitative dependence is not known. Although this mechanism remains as a possible explanation for the dependence of activation energy on exposure, the present data show no simple correlation between solubility of the silver halide in the developer (as varied by addition of bromide or sulfite) and the activation energy.

The dependence of the activation energy on the amount of exposure may be quite general. Some dependence was observed by James and Vanselow[6] in development by 1-phenyl-3-pyrazolidinone at pH 6.5 where diffusion was not rate-controlling. A dependence also was observed with various hydroquinone developers in connection with the present work, although the dependence was not as great for hydroquinone as for Metol.

The dependence of activation energy on exposure influences the form of the characteristic curve obtained at any stage of development, and influences the dependence of the shape of that curve upon the temperature of development. The change in the shape of the curve with change in temperature is qualitatively that expected from the activation energy–exposure relation. A quantitative treatment would involve considerable difficulty, however. In any particular exposure step, the grains in the lower depths of the emulsion receive less exposure than those near the surface. Each exposure step, therefore, represents a range of effective exposures of the grains in that area of the coating, and this would have to be taken into account in a quantitative treatment of the effect of temperature on curve shape.

The increase in activation energy with decrease in exposure causes the toe speed to increase with temperature for development to a given gamma, or to any fixed density on the straightline or shoulder portions of the curve. The increase in speed, however, is at the expense of an increase in fog, since the activation energy of fog formation is higher than that of image development.

As the pH of the Metol developer is increased, a point is reached where diffusion of the developer into the emulsion becomes largely rate-controlling for development of the heavily exposed areas beyond the induction period. The rate of development shown in the toe region of the curve is still largely controlled by the rate of the chemical reaction. This transition is accompanied by an even more pronounced relative flattening of the shoulder of the characteristic curve. This state of affairs is reached with the Metol developer at a pH of about 9.5 and a temperature of above 40 C when the developer contains no added bromide. It is reached at 20 C or below when the pH is 10.75, even if the developer contains 1 gram of potassium bromide per liter.

Acknowledgment

References

1. W. B. Ferguson and B. F. Howard, Phot. J., Vol. 45, p. 118 (1905); W. B. Ferguson, Brit. J. Phot., Vol. 54, p. 337 (1907).
2. Cf. C. E. K. Mees, Theory of the Photographic Process, Revised Edition, The Macmillan Co., New York, N. Y., 1954, p. 658.
3. R. W. Henn and J. I. Crabtree, J. Phot. Soc. Am., Vol. 12, p. 445 (1946).
4. L. J. Fortmiller and T. H. James, PSA Journal (Phot. Sci. and Technique), Vol. 17B, p. 102 (1951); Vol. 18B, p. 76 (1952); Vol. 19B, p. 109 (1953).
5. L. J. Fortmiller and T. H. James, R.P.S. Centenary International Conference on the Science and Applications of Photography, London, Sept., 19–26, 1953; J. Soc. Motion Picture and Television Engrs., Vol. 62, p. 251 (1954).
6. T. H. James and W. Vanselow, Phot. Science and Technique, (II) Vol. 1, p. 77 (1954).
7. T. Uryu, J. Soc. Sci. Phot. Japan, Vol. 14, p. 4 (1951).
8. S. Sugai and J. Furuichi, J. Phys. Soc. Japan, Vol. 8, p. 681 (1953); S. Sugai, Symposium on Photographic Sensitivity, Hakone, Japan, 1953.
9. Cf. J. A. Smibert and M. O'Bern, R.P.S. Centenary International Conference on the Science and Applications of Photography, London, Sept. 19–26, 1953.
10. J. E. LuValle, F. M. Dunnington, and C. Margnetti, Private Communication.
11. G. I. P. Levenson, J. Phot. Science, Vol. 1, p. 117 (1953).
12. T. H. James, J. Franklin Inst., Vol. 240, p. 83, 229 (1945).
13. T. H. James, PSA Journal, Vol. 13, p. 608 (1947).
14. G. I. P. Levenson and T. H. James, J. Phot. Science, Vol. 2, p. 169 (1954).

RESULTS OF A STUDY ON OFFSET COLLOTYPE

Harry H. Lerner*

T HE PROCESS commonly called "photo-gelatin" or, preferably, "collotype" has been in the hands of printing craftsmen for some fifty years. The literature on the subject is exceedingly sparse and whatever is available fails to disclose many of the important techniques used in the process. It is therefore not surprising that little is known about collotype and few people in the Graphic Arts Industry have taken an interest in this unique method of printing.

Collotype is the only photo-mechanical method which is capable of printing a continuous-tone, screenless image. Another distinguishing feature of collotype is the exceptional tonal quality which it is capable of yielding. Its chief disadvantage, of course, is its short run of very uncertain duration. It might be well to review briefly the basic aspects of the collotype printing method so that the process will be clear to those who are meeting it for the first time.

Basic Principle of Collotype

Just about a hundred years ago a Frenchman by the name of Poitevin† discovered the basic principle of Collotype, namely, that a bichromated colloid such as gelatin was light-sensitive and could cause a reaction to take place which tanned the colloid in direct ratio to exposure. This is not only the basis for Collotype—it is also the basis for almost every photo-mechanical printing method practiced today. But the unique property of the bichromated colloid has been largely overlooked in all the screen methods such as Photo-engraving and Lighography. Only in Gravure and Collotype do we take advantage of the unusual straight line reproduction curve which a bichromated colloid is capable of yielding.

Briefly, the mechanism of Collotype is the following: gelatin is sensitized with sodium dichromate and the resulting solution is coated on a support. The plate thus formed is exposed under a continuous-tone negative and an image is created in accordance with the light modulated by the negative densities. When the plate is placed in water and the bichromate sensitizer is washed out an image is left in the gelatin layer that is composed of relatively hard and soft gelatin. The picture areas representing shadows are, of course, highly tanned while the middle tones and highlights are relatively less tanned. If the gelatin layer is swelled in a glycerine and water bath it is quite obvious what will happen. The image will take up glycerine and water, in exact proportion to the amount of tanning produced by the light which passed through the negative on exposure. When this image is inked on the press, those areas which are very

hard, such as the shadows, will accept ink readily while the less tanned areas will accept less ink and the highlights will actually repel most of the ink. All that is left is to transfer the inked image to a sheet of paper. Normally, this is done by Direct Rotary lighographic presses which are now considered the relics of the printing industry. In Europe, flat-bed presses are still used and, instead of coating a sheet of aluminum for the plate as we do, they coat a heavy piece of plate glass. The process, however, is essentially the same. The paper comes in direct contact with the plate and pulls the ink image out.

The Collotype process is exceedingly simple and straightforward. When it was introduced in this country more than fifty years ago, Collotype was surprisingly successful almost immediately. Yet hardly any technological advances were made in Collotype in all these years with possibly one exception. Around 1930, the Direct Rotary press was introduced for a Collotype plate and this was a great improvement over the European flat-beds. A press run of 500 impressions per day for a flat-bed press was considered average while the Direct Rotary under ideal conditions could produce ten times that amount or around 5000 impressions which is just about the limit for the gelatin plate.

By the late 1930's, the need for longer press runs was dictated by developments in American business. Highly organized national distribution set-ups required widespread advertising coverage and this in turn gave rise to commercial printing which could adequately fulfill those needs. The Collotype printers, flushed with the success of the Direct Rotary press, took the next logical step and put the Collotype plate on an offset press. But the high hopes soon vanished and by 1940 or thereabouts the offset presses had proven to be a failure for Collotype printing and were discarded.

The offset *press* was at fault—for the Collotype printers never blamed the plate, which had always given them such excellent results, and it was natural for them to find fault with the offset principle rather than with their chief stock in trade. Why did these initial experiments fail? I cannot give you any first hand information on the answer to that question as I was not connected with any of the three firms that had put in offset presses. But a number of our employees actually took part in the experiments. This is what they report in more or less their own words:

1. The shadow detail was poor and after a few thousand impressions they were completely closed up and clogged.

2. Never could run enough ink to get even a fair black — prints had a dull grayish look.

3. Fine detail was very often fuzzy and unsharp.

4. Press had to be stopped and plate dampened much too often.

5. Gear streaks and roller marks were difficult to eliminate.

6. Color work was flat and required many more extra colors.

This is a rather imposing list of objections and it was evidently more than could be handled so one could not blame them for giving up.

Aerial Photograph Reproduction

Some two years ago, Messrs. Robert E. Rossell and Stephen W. Gibson of the Engineer Research and Development Laboratories at Fort Belvoir began to study continuous-tone printing for purposes of reproducing the fine detail of aerial photographs. Visits were made to all the Collotype plants and very little information was forthcoming which could conceivably be encouraging.

Their requirement of a minimum 10,000 run from a plate sounded like a fine dream. It was the experience of Triton Press that runs over 5000 impressions were exceedingly rare and to double that figure as a minimum requirement was indeed very ambitious, to say the least. Plates wear out principally because of the abrasive action of the paper in contact with the plate surface. And since the gelatin emulsion is of necessity composed of hard and soft areas comprising the image and non-image portions, the relationship of soft to hard gelatin cannot be changed to any great degree. Consequently, the soft areas representing the highlights of the image as well as the non-image eventually break down. In the offset press this situation is not as drastic since only the rubber blanket touches the plate. However, considerable pressure must exist between blanket and plate to pull out a heavy deposit of ink from the shadows. The highlights, being swollen with moisture, will take the brunt of the impact from the blanket and will finally break down although not as rapidly as from direct contact with paper.

Therefore, the emphasis for this study was directed toward improving the plate coating which is exactly what the earlier experimenters with Offset Collotype failed to do.

Experience gained during World War II showed that the need existed for large quantities of aerial photographs to supplement, and in some cases to bring up to date, existing topographic maps. For the reproduction of continuous-tone subjects such as aerial photographs the topographic units of the Army were equipped, during the early part of the war, with 133 line glass halftone screens. The 300 line magenta contact screen was developed during the war in conjunction with the Corps of Engineers and screens of that type were issued to the topographic units as soon as available. A 70-lb. substance coated stock was also issued, in addition to the high wet strength map stock, to be used for halftone reproductions.

It can be seen from the foregoing that every attempt was made, under the pressure of war, to provide for the best possible reproduction of aerial photographs and photomaps. However, the never ending search for 'something better" lead to the investigation of Collotype. The ability to provide the troops in the field with up-to-date, high quality reproductions is extremely valuable, for, no matter how intensive the training in map reading, a photograph or reasonable facsimile is always preferred over a topographic map. In some areas, too, up-to-date maps do not exist and reproductions from aerial photographs may be all that is available.

It was also decided to make the program as broad as possible in the hope of striking a lead that could logically be pursued. The objective of the contract that was finally awarded to Triton Press, Incorporated, New York City, by the Engineer Research and Development Laboratories, Corps of Engineers, U. S. Army, Fort Belvoir, Virginia, was, however, very clearly defined; namely, to find a practical method to print at least 10,000 copies of aerial photographs in screenless, continuous-tone. The catch, of course, is in the word "practical"—and what could be more practical than to make it a pre-sensitized plate. So, the list of requirements began to multiply and the program became broader and broader. Here is a partial list of subjects which had to be investigated: 1. Pre-sensitized plates; 2. Pre-coated, unsensitized plates; 3. Gelatin substitutes; 4. Sensitizers; 5. Inks; 6. Tanning agents; 7. Humectants; 8. Non-metallic supports; 9. Effects of humidity and temperature, and so forth.

But, as time began to run out there had to be concentration in the area of maximum experience and skill which is why Triton Press finally settled for a bichromated colloid that is essentially gelatin. Perhaps it is a happy coincidence that gelatin was chosen. The chemistry and gel-forming ability of gelatin has been extensively investigated in the last twenty or thirty years so more is known about this protein than about any other protein. Due to this knowledge the commercial standardization of gelatin is further advanced than that of any other commercial protein.

The high average molecular weight of gelatin—about 100,000—is partly responsible for the high mechanical strength of gelatin films. The outstanding ability of gelatin to form reversible gels, to hold water and plasticizers in the gel lattice, to crosslink with a number of chemical crosslinking agents; are all essential requirements for the Collotype plate. Other natural proteins such as albumen, casein, zein have been tried but do not possess the high mechanical strength and gelling properties of gelatin.

However, despite the overwhelming advantages of gelatin, it is by no means the only colloid that could be used. Synthetic high polymers have been suggested, such as Polyvinyl Alcohol, Polyacrylamide, Polyvinylpyrrolidone, and many others alone and in mixtures. While these synthetic polymers do have certain advantages over gelatin, they cannot replace gelatin until they are superior not only in one but in all the requirements for a good Collotype coating. Such a synthetic colloid will, therefore, have to be "tailor-made" to combine in one product all the advantages over gelatin.

The choice of bichromate as the sensitizer has also been one of expediency. While the bichromate is highly satisfactory from the standpoint of image-formation and characteristic curve, it is low in quantum yield or, as the photographer would put it, slow in speed. It has recently been reported (Oster, Photochemistry of Dyes in Solution, Photogr. Eng. 4, 173) that certain water soluble vinyl monomers can be polymerized by light and the quantum yield is of the order of one million as compared, for example, to the conventional silver halide system which has a quantum yield of less than one. Of course, with silver halide the action of development serves to intensify the image so that the quantum yield is increased many millions of times. It would be highly desirable to have the speed of a silver sensitized material and we have

accumulated sufficient evidence to show that a silver halide, pre-sensitized plate is indeed a possibility.

Collotype Plate Requirements

Although gelatin may not be the ideal substance it is nevertheless a material which can be modified over an exceedingly wide range of conditions. Consider for a moment the paradoxical requirements of a Collotype plate. It must be sufficiently soft to absorb large amounts of moisture. The degree of swelling is, of course, dictated by the exposure in image areas where crosslinking takes place under the influence of light. Highlights and non-image areas or pure whites must swell and accept maximum moisture to repel all ink and print as whites. At the same time, these areas—highlights and whites—must have high mechanical strength. But gelatin in a swollen state exhibits the least strength and therein was the problem.

Fortunately, there are an exceedingly large number of humectants and tanning agents for gelatin and by combining these crosslinking chemicals a balance was established to circumvent to a large degree this so-called paradox. · The plate coating today is exceptionally tough and yet its swelling properties have not suffered— a condition which was formerly considered impossible to obtain. The result, therefore, is a plate that is capable of long runs without sacrificing quality.

A group of negatives was assembled with widely differing gradient characteristics. In this case aerial negatives supplied by the Army—some were low altitude, well exposed shots while others were taken under poor lighting conditions at higher altitudes and exhibiting the usual faults in aerial negatives. The four negatives chosen were printed by Direct Rotary Collotype—by Offset Collotype—and by 300 line Conventional Offset.

The Direct Rotary prints represented the best one could hope to attain—and the 300 line Conventional Offset prints became the lowest limit of quality which we would have to surpass. By making these comparisons we established a frame of reference in which to operate.

The water fountain, it must be pointed out, is never used in Offset Collotype. The colloid of the plate acts as a reservoir by taking moisture from the air. To maintain this moisture balance it is necessary to control the humidity in the pressroom. The usual procedure in Direct Rotary Collotype is to stop the press every five or six hundred sheets and sponge the plate with glycerine and water. On an Offset press that is running at a speed of 5000 an hour this would mean stopping the press for dampening every 8 minutes which would be out of the question from a practical standpoint. So a way had to be found which would slow down the moisture exchange between the plate and the surrounding air. The blanket is also a source of moisture loss but time was not available to study that particular phase, although it would certainly be worth while.

The plate we have today will run about three to four thousand prints before dampening becomes necessary with the glycerine and water solution. It doesn't seem to matter much any more whether the press is run at 3M per hour or 5M per hour—if uniformly high quality is maintained one must replace the glycerine in the plate about every 3500 sheets.

Another point which might be worth mentioning is the kind of negative most suited to the process. Fortunately it is a very low contrast negative and in high speed, high altitude aerial photography that's the type of photograph that is obtained most of the time. These negatives have a density range between 0.8 and 0.9 with the shadow step around 0.25 to 0.30 and the highlights about 1.10 to 1.20 maximum. Regardless of the density range the over-all density cannot be too heavy, otherwise exposures become too high with the result that shadows get too deep and it will be almost impossible to wash out the bichromate from those areas. If the bichromate sensitizer does not wash out, the shadows will continue to harden and by the time the plate goes on the press, the shadow areas will be clogged and will not press out properly. This is the chief danger in long exposures.

A very large degree of control is provided on the press. By raising the moisture in the room contrast is increased and vice versa. An area which is somewhat underexposed and prints too light can be brought up locally by the use of tanning agents such as tannic acid and alcohol. The same is true for clogged shadows. By applying ammonia or sodium sulphite, the shadow can be opened up quite easily. To get rid of a tint or even a mistake such as a break-through on the mask, a weak solution of triethanolamine is enough.

One other factor which should be considered is the ink used in Collotype. As a rule, the stiffer the ink the greater the contrast in the print while the softer the ink the more tone and gradation will be obtained. However, the chemical composition of the ink vehicle will have as much bearing on printing quality as the physical characteristics. This phenomena was demonstrated conclusively in the course of this investigation.

Pre-sensitized Silver Plates

Some mention was previously made of experiments with a silver halide pre-sensitized plate. Coating a silver emulsion on aluminum was considered impractical. Unless the surface of the aluminum is made chemically inert, the silver emulsion will develop spots and fog. Since photographic manufacturers are geared to coat sensitized goods on a web, it was felt that a plastic material that can be made in rolls would be more suitable as a support. Film base, even the topographic variety, is not dimensionally stable enough to withstand the high moisture and glycerine to which the plate is subjected. Although printing was done quite successfully from a vinyl support, the plate very often shattered in the press if there was the slightest nick on one of the edges. Brittleness of the vinyl could be overcome by plasticizers but that only introduced other obstacles such as elasticity under stress and "cold flow". It is hard enough to get good register in printing without having the plate stretch while the press is running. The problem was finally licked by using a laminate that stood up remarkably well. By sandwiching a pre-treated glass cloth between two sheets of polyvinyl chloride a support was produced that was dimensionally stable, had excellent moisture resistance, and was chemically inert to the emulsion. It was not brittle and could resist enormous stress of the plate clamps without shattering.

In conclusion, I should like to say that despite early

misgivings and doubts concerning the feasibility of a 10,000 run with Offset Collotype, runs far beyond that figure were finally realized. Prints made after a 25,000 run have shown no appreciable loss in quality.

Observations based on long experience with Collotype were studied and correlated to evolve an arrangement of plate formula and press technique that has proven to be superior to anything encountered in the past. But what

is more revealing is that, although the surface has only been scratched, there are enough signs to point the way toward making Offset Collotype a *practical* method for printing in continuous-tone.

The present plans are for the Map Reproduction Branch of the Engineer Research and Development Laboratories to evaluate this process now to determine its feasibility for military map reproduction.

REPRODUCTION USING BROMIDE PAPER FOR NEGATIVE MATERIAL

M. Maher-Moussa*

X-RAY TECHNICIANS usually use X-ray sheet film, cut to size, when photographing negative X-ray films for making an intermediary small-sized positive to be contact-printed for a final negative on glossy paper.

X-ray film used as negative material for this purpose usually gives flat results, since it is a rather soft fast emulsion. Process plates were tried but gave too contrasty results in which weak detail was lost. Medium speed negative materials gave satisfactory results, but as paper was much cheaper than both films and plates, it was tried as a substitute.

The main difficulty with paper was opacity and coarse grain. Soft single-weight glossy bromide paper was used. It was cut to size (an easy operation with paper) and inserted in the metal sheaths instead of sheet film, to photograph the X-ray films, illuminated from behind.

The final negative print had to be made from the intermediary positive paper by contact printing, after "oiling" the back of the latter in order to render it translucent. A sheet of Kodapak Diffusion material (0.003 inches) was interposed so that grain would be reduced still further. This was put with its matte surface next to the emulsion side of the oiled positive and the latter printed, emulsion to emulsion, with the final negative paper. The results so obtained equalled without any loss of quality those employing intermediary film or plate material.

The secret lay in the particular nature of the oiling mixture used. The idea is of course not new, but methods previously recommended, like waxing and the use of Canada balsam, were tried with results much inferior to those attained by the formula finally arrived at.

Waxing (with paraffin wax) was very messy indeed and yielded poor results. The following methods were tried, the optimum aimed at being a lasting *maximum* translucency:

(1) The poorest results were obtained with one part (by weight) of either dry or syrupy Canada balsam in 5 parts turpentine. The translucency was transient, as the paper base turned opaque in half an hour.

(2) Next was a mixture of equal volumes of castor oil and ether (recommended by Dr. Max Thorek in his book "Camera Art").

(3) Then a mixture of 3 volumes cedar-wood oil (for microscopic use) and 1 volume turpentine.

(4) A similar result was obtained from a mixture of equal parts of thin machine oil and acetone.

(5) A better result was given by 1 volume of thin machine oil mixed with three volumes of xylol. Oil alone took 3 days to dry and yielded poor results. Xylol alone or turpentine or household petrol, evaporated much too quickly to be of any practical value.

(6) Almost identical results were obtained with the tricresyl phosphate 50 volumes, petrol 49 and acetone 1 mixture, recommended in the British Journal Photographic Almanac 1951 page 288.

(7) A slightly better result was obtained with 3 volumes linseed oil to 1 volume turpentine.

(8) The best result as judged by maximum translucency which lasted permanently, was obtained when 3 volumes of thin machine oil (Kalle super oil for machines or Slipco general purpose oil) were thinned with 1 volume of turpentine. This was applied to the back of the intermediary paper (with a wad of cotton-wool) after it had been washed and dried. Any thin machine oil so thinned, would probably do. A photoelectric exposure meter was used for comparing the degree of translucency in the various formulae tried.

Cheapness is not the only advantage in using bromide paper instead of films or plates. The slowness of paper makes easy the shading of excessively thin areas in the original X-ray film while the film is being reproduced; a piece of black paper held on a wire is kept on the move next to the illuminated x-ray film. Again, thin areas on the intermediary paper positive can be more easily dealt with by applying to the emulsion side, before oiling the back, a red dye like Neococcine, or Winsor and Newton's Photo Tints.

The method is also applicable to line work, though the results are inferior to reflex document contact printing. When the method was tried in reproducing half-tone pictorial prints, the results were indeed very satisfactory as long as the intermediary paper-negative was used for contact printing and not for enlarging. Soft grade thin (single-weight) paper is essential and should neither be developed in a contrasty developer, nor developed to finality, as the method is inclined to give results on the constrasty side.

It is fair to admit that though quick, simple and economical, the method is not intended to replace the "highlight masking process" used in the U.S.A. The latter undoubtedly gives superb results, but is lengthy, complicated and expensive.

* Chief, Department of Clinical Photography, Faculty of Medicine, University of Alexandria, Egypt. Received 17 January, 1955.

WORLD-WIDE PHOTOGRAPHIC STANDARDS, OBJECTIVE OF STOCKHOLM MEETING

J. W. McNair*

PHOTOGRAPHIC EXPERTS from ten countries have organized a meeting in Stockholm, Sweden, early in June 1955 to act on recommendations for the adoption of international standards for photography. Fifteen additional countries, that had previously signified their interest in the establishment of international standards for photography, have been asked to participate as observers.

These twenty-five nations, through their respective national standards organizations, will be the guests of *Sveriges Standardiserings Kommission*, the Swedish national standards body. Dr. Hilding Törnebohm, President of the INTERNATIONAL ORGANIZATION FOR STANDARDIZATION (ISO), has invited that organization to hold its 1955 General Assembly and Council meetings in his native country June 6 to 18. Some dozen technical committees of the ISO will hold their meetings in Stockholm during the same period of time.

The American Standards Association has been assigned the Secretariat for ISO Technical Committee 42 on Photography and will participate in the Stockholm meeting in two ways. Functioning as the Secretariat, the ASA called the meeting for five days, June 6 to 10 inclusive, made secretarial provisions for the sessions, circulated technical documents for study prior to the meeting, set up a tentative Agenda, and will provide staff assistance during the meeting.

As one of the ten national standards bodies that comprise the active (participating) membership of ISO/TC 42, the American Standards Association has organized the USA delegation to the Stockholm meeting, provided the participating nations with copies and drafts of American Standards that are being proposed by this country for adoption as international standards, and arranged for study by photographic experts in the United States of draft proposals submitted by other countries in advance of the international meeting.

Mr. Marion E. Russell, FPSA, of the Eastman Kodak Company, Rochester, New York, who is a member of the Photographic Standards Board of the ASA and a former chairman of Sectional Committee PH2 on Photographic Sensitometry, has been selected as leader of the delegation from the USA to the Stockholm meeting.

American Standards Proposed for International Adoption

Two American Standards in the field of photography have already been adopted† by the International Organization for Standardization as ISO Recommendations. ISO/R5 "Diffuse Transmission Density" is substantially identical with American Standard Z38.2.5-1946 having the same title. ISO/R6 "Method for Determining Photographic Speed and Exposure Index" is based on American Standard PH2.5-1954 and an earlier version of the same American Standard Method for Determining Photographic Speed and Exposure Index.

The Stockholm meeting will consider over 20 American Standards for photography with regard to their suitability as international standards. These standards cover the field of photography rather broadly. Some, like the specification of "safety film," are fundamental in nature. Others, such as photoelectric exposure meter characteristics, or specifications for films intended for permanent records, or the dimensions of stereo pictures, are more specific. Quite a number deal with dimensions and tolerances which govern fit and interchangeability. Standards for roll films of various size and camera standards for the position of back windows (peepholes) and picture sizes on roll film, fall into this category. Some deal with standard methods of test, like the test for residual hypo in photographic layers or tests for classifying the internal synchronization of front shutters on cameras. There are six commodity specifications establishing the requirements and test methods for "photographic grade" chemicals commonly used in processing photographic sensitized materials. Simplification, by the elimination of unnecessary items, is involved in some of the proposals, like the one dealing with standard exposure time marking on camera shutters or the standard distance scales for camera lenses.

Other countries have proposed some of their national standards for consideration as international recommendations. The British Standards Institution has developed a proposal for the identification of different emulsion types of amateur roll films by the means of specific colors of backing paper. The German standards organization, *Deutscher Normenausschuss* (DNA) is offering a German proposal for the dimensions of 35mm daylight loading magazines for miniature camera use for consideration and comparison with previously proposed American Standards. It is anticipated that delegates from other countries will bring to the Stockholm meeting additional national standards of their respective countries to be considered by the international committee.

Nations Interested in Photographic Standards

The active or "participating" members of ISO Technical Committee 42 on Photography include, naturally, the countries in which photographic industries are factors of importance in the national economy. These are Austria, Belgium, Czechoslovakia, France, Germany, Italy, Netherlands, Union of Soviet Socialist Republics, and United Kingdom, in addition to the USA, as Secretariat.

In addition to the countries which signified their desire to actively participate in the work of the international committee of standards for photography, fifteen other nations wished to keep in touch with the work of ISO/TC 42 as (O) or "observer" members. Such members receive copies of all correspondence and may attend meetings but do not participate actively in the technical work. The (O) members of ISO/TC 42 are Australia, Canada, Chile, Hungary, India, Japan, Mexico, Poland, Portugal, Roumania, Spain, Sweden, Switzerland, Union of South Africa, Uruguay, and Yugoslavia. Under ISO rules, membership under either category is voluntary.

ISO Leadership in World Standards Activity

The INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, and to a lesser extent its predecessor ISA (International Standards Association) which was dissolved during World War II, have largely supplanted other agencies that formerly worked toward the establishment of international standards. Some international groups continue to operate, like the International Electrotechnical Commission, but their activities are coordinated with ISO.

In the field of photography, considering the international aspects of standardization, ISO has continued, expanded and made effective the work that was pioneered by the VIIIth (1931, Dresden) and IXth (1935, Paris) meetings of the International Congress of Scientific and Applied Photography. The approval of ISO/R6 Method for Determining Photographic Speed and Exposure Index as an international recommendation was not a unique accomplishment in the field of photographic sensitometry. It was the culmination of international thinking, cooperation, and technological advances that were inspired by and fostered during the period from 1925 to 1935 by the International Congress of Scientific and Applied Photography. That organization, which existed primarily for the exchange of ideas and information about the science of photography, had no executive power and no standards program, but it did provide an opportunity for international discussion of technical problems that have in recent years been found susceptible to international standardization.

This forum passed out of existence following the 1935 meeting in Paris. A meeting planned for Warsaw in 1940 never came about, for historic reasons, and the Congress, following the end of World War II was effectively replaced by other international gatherings of photographic scientists, such as the Symposium on Fundamental Mechanisms of Photographic Sensitivity held at the University of Bristol in England, March 1950, and the Colloquium on the Sensitivity of Crystals and Photographic Emulsions, held in Paris in September 1951.

The ISO, transformed from the old ISA, through the metamorphosis of World War II, emerged in 1946 into a world newly impressed with the need for international understanding and unity. The resumption of trade between countries brought new realization of the need for international standards. By the end of 1954, there were eleven ISO Recommendations in effect, and two of them, as mentioned above, are in the field of photography.

In January 1955, the ISO had 55 Draft ISO Recommendations in various stages of the procedure necessary for approval as international standards recommendations. Seven of these were in the motion picture field and one was concerned with photocopy paper sizes for document reproduction. Nineteen additional Draft ISO Recommendations in the field of motion pictures were being made ready for distribution to the 35 countries which are the Member Bodies of the ISO.

Other International Standards Meetings Concerning Photography

Prior to the Stockholm meetings June 6 to 12, 1955, there will be a meeting in Paris June 2, 3 and 4 of Subcommittee No. 1 on Photographic Documentation of ISO Technical Committee 46 on Documentation. The Subcommittee on Photographic Documentation operates under the supervision of the French standards organization *Association Française de Normalisation* (AFNOR). Some of the American delegates to the Stockholm meeting of ISO/TC 42 on Photography expect to arrive there via Paris where they will attend the sessions on Photographic Documentation.

This committee is concerned with quality criteria for processed microfilms, with performance specifications for microfilm readers, with preferred sizes for microfilms and opaque microtext, with test methods for microfilm cameras and readers, and similar matters.

Following the meeting of ISO/TC 42 in Stockholm, there will be a meeting at the same place of ISO/TC 36 on Cinematography. The ASA holds the Secretariat for the international standards committee for motion pictures, TC 36, just as it does for the photographic Technical Committee 42. Several of the delegates to the meeting of ISO/TC 42 will also be members of the delegation representing the USA on the following meeting of ISO/TC 36.

This will be the second meeting of the Technical Committee on Motion Pictures. The group held its first international meeting in New York City in June 1952. Delegates from Canada, France, Germany, United Kingdom and the USA attended at that time and there were observers from Belgium and Switzerland. Meanwhile twenty-two Draft ISO Recommendations for international standards that had developed from this 1952 meeting have been prepared and turned over to ISO headquarters for action by the Member Bodies.

The Agenda for the second meeting in Stockholm of ISO/TC 36 on Cinematography, June 11, 13, 14, 15, and 16, 1955, includes six technical subjects that were not covered by the 1952 meeting. Some of these new items for international consideration involve the dimensions and location of magnetic sound tracks on motion picture film and the reproduction characteristics of magnetic sound tracks. Of interest to exhibitors as well as producers of motion pictures will be discussions concerning standards for screen brightness levels (which have a bearing on the density of prints released by exchanges for exhibition) and the dimensions of wide screen motion pictures.

The American delegation to the Second Meeting of ISO/TC 36 will be headed by Dr. Deane R. White, Research Director for the Photo(graphic) Products Department of E. I. duPont de Nemours and Company. Dr. White had previously served as leader of the USA

delegation to the first meeting in New York in 1952. The meeting, when it convenes in Stockholm June 11th, will be presided over by Mr. Axel Jensen of the Bell Telephone Laboratories in Murray Hill, New Jersey. Mr. Jensen is Engineering Vice-President of the Society of Motion Picture and Television Engineers who are Sponsors for ASA Sectional Committee PH22, the technical Committee in this country for the development of national and international standards for motion pictures and for cinematographic aspects of television.

PHOTOGRAPHIC TECHNIQUES AS APPLIED TO THE STUDY OF HIGH-SPEED FLOW

John F. Darsow*

T HE PURPOSE of this paper is to describe some of the techniques of making high-speed air flow visible and methods of photographically recording the flow phenomena. The term "high speed" in this case refers to air velocities near and above the speed of sound. At these speeds the compressibility of air is of fundamental importance, and large changes in density occur. The aerodynamicist can study the high-speed flow past objects by investigating these density changes. Since any change in air density will cause a proportional change in the index of refraction, a light beam passed through a region of varying density will be deflected by varying amounts and can be used to visualize the flow. This phenomenon is the basis of the shadowgraph and schlieren flow visualization techniques.

The Shadowgraph

The shadowgraph[1] is a very simple but effective device. Light from a small source is projected through the air and the density gradients in the air deflect the light and cast a pattern on a screen. Figure one shows a simple shadowgraph system. The wing panel is mounted on one wall of a wind tunnel. A beam of light is projected from the opposite wall. Dark shadows on the illuminated wall indicate the location, in the high-speed flow past the wing, of shock waves, which are regions across which there are abrupt changes in air density.
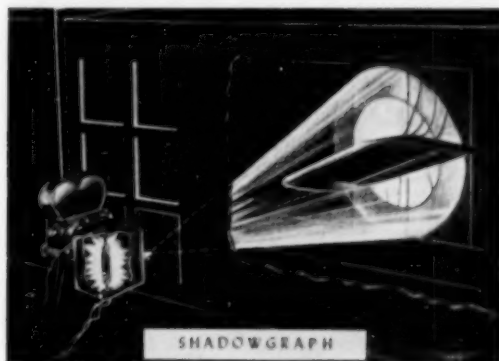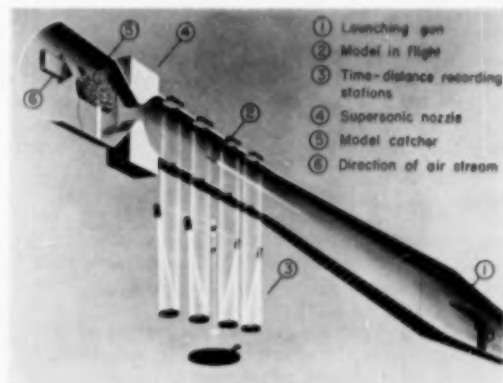

Fig. 2. Supersonic free-flight optical system providing a four station shadowgraph system which, together with a chronograph, provides time-distance data on objects moving against an airstream with effective velocities up to ten times the speed of sound.

A more refined shadowgraph application is used in the Ames supersonic free-flight wind tunnel[2] as illustrated in Figure two. Air flows from left to right at supersonic speeds. Models are fired from a gun into the oncoming airstream. The combined air and model velocity creates effective speeds as large as ten times the speed of sound. The time-distance history of the flight is recorded by these stations as the model flies through the test section, and from this the forces acting on the model can be evaluated. In this wind tunnel the time-distance history is obtained by using a four station shadowgraph and a chronograph.

The operation of this equipment is more easily followed by considering only one of the shadowgraph stations as shown in Figure three. As the model approaches the station it encounters a light beam which projects through the tunnel onto a photoelectric cell. The

Fig. 1. The Shadograph method for photographing density differences in an air stream moving at or near the velocity of sound. An object mounted on one wall of a wind tunnel is illuminated by a light source of small area but high intensity through a window in the opposite wall. Shock waves in the air stream cast dark shadows which can be photographed.
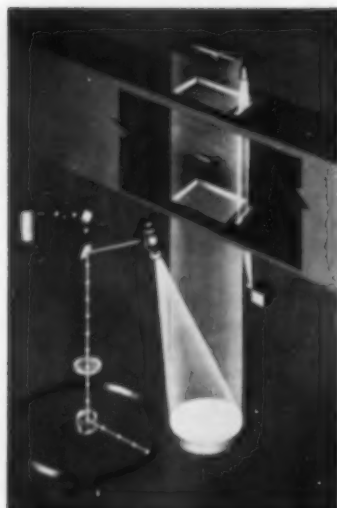
Fig. 3. Closeup of a single shadowgraph station from Fig. 2 showing the light beam and photoelectric cell trigger which actuates the spark source after a pre-determined time delay.

model's shadow modifies the output of the cell and this triggers a spark source after suitable time delay. Condenser discharge spark light sources are used in order to obtain the exposures of about one micro-second needed to get sharp pictures of the models. When the spark is triggered part of the light escapes from the side of the spark housing and is reflected by a mirror to a rotating prism which in turn reflects the light to the film on the periphery of the chronograph. To provide a time base, light from a mercury arc lamp pulsed at 20,000 cycles per second is projected on the chronograph film. A comparison of these two records gives a time history of the flight.

The light from the spark sources is collimated by the use of spherical mirrors to prevent image distortion, and parallel light shadowgraphs are recorded on photographic glass plates, which are used to permit the utmost accuracy in the measurement of model position. To prevent fogging of the plates by scattered light from the adjacent photobeam a red blind film is used in conjunction with a red filtered photobeam light source and a red-sensitive vacuum phototube. A typical shadow-
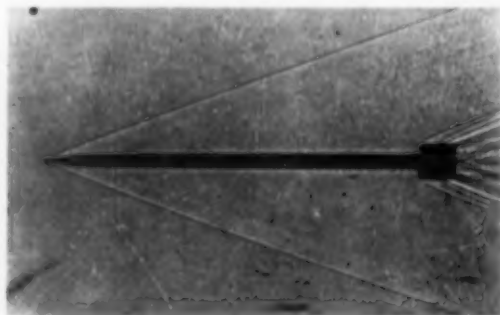

Fig. 4. Typical shadowgraph with shock waves appearing as dark lines.

graph is shown in Figure four. The dark lines are shock waves. The bright region adjacent to the model is air retarded by friction forces—called the boundary layer.

Studying Spinning Motion

In addition to the shadowgraphs used to study the longitudinal motion of models it is of interest to measure the spinning motion. To obtain this information a Fastax camera is located at the model catcher and the oncoming model is photographed by way of a 45-degree diagonal mirror. To obtain adequate depth of field and magnification Fastax movies are taken with a 17-inch focal length lens at f/60. The model is back illuminated by a single press-type flash bulb, which provides adequate illumination since the time of the model's flight is shorter than the duration of commercial flash bulbs. The bulb is timed to fire at the instant the model leaves the gun.

Vapor Screen

Another interesting high-speed flow visualization system developed at the Ames Laboratory is the vapor-screen technique. Water vapor is introduced into the wind-tunnel airstream upstream of the test section. In passing into the test section, the air drops in temperature and
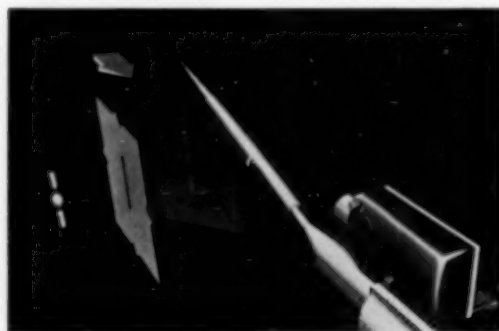

Fig. 5. Vapor screen equipment arranged so that a thin section of the fog-filled chamber is illuminated through a slit.

water vapor condenses to form a uniform fog. A high intensity light source, as shown in Figure five, is placed behind a slit, allowing light to pass through the wind tunnel and uniformly illuminate a thin plane of the fog. Flow disturbances, such as vortices, then alter the uniformity of the fog. Figure six shows vortices which have been shed from the wings of a model.

Schlieren Photography

The most sensitive flow visualization technique available is the schlieren system. The schlieren technique is discussed in detail in reference 3. A typical schlieren system is illustrated in Figure seven. Light from a line or point source located at the focal point of a lens or
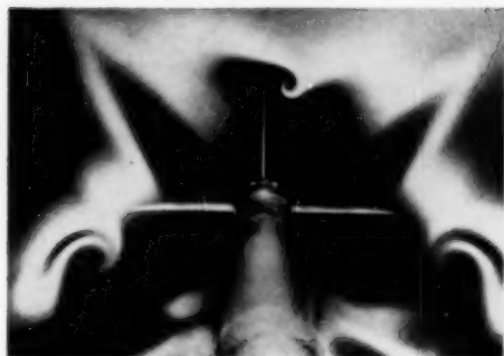
Fig. 6. Vapor screen photograph showing disturbances in a thin section of illuminated water vapor.

Fig. 7. Mirror schlieren optical system. Light from a point source, S, is collimated by mirror, M_1, then passed through the test section to an identical image-forming mirror, M_2, which recreates at its focal point an image of the light source slit. A knife edge at the focal point, f.1 can be adjusted to control the intensity on the viewing screen.

parabolic mirror is collimated and passed through the test section to an identical image-forming mirror or lens. (The mirror-schlieren system is most common, since well-corrected lenses of apertures greater than six inches are prohibitively expensive.) The image-forming mirror collects the bundle of parallel light and recreates at its focal point an image of the light source slit. A simple knife edge is then located at this image. If this knife edge is adjusted to traverse the image, the intensity on the view screen can be uniformly controlled from "bright field" (knife edge removed) to dark field (knife edge obstructing the image). Adjustment of the knife edge acts in a manner similar to a lens iris. An undisturbed ray of light passing point P will arrive at p^1 through the knife-edge image point. However, should a density gradient occur at P the ray will be deflected in proportion to the gradient. This ray will then arrive at the screen at p^1 but will pass some distance below the knife edge and image point. If the knife edge is adjusted to partially darken the field the deviated ray will create a bright point on the screen at p^1. The sum of all deviations in the field will then contribute to a composite image of the deviated rays.
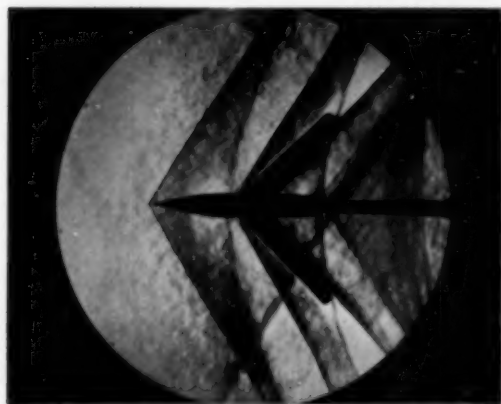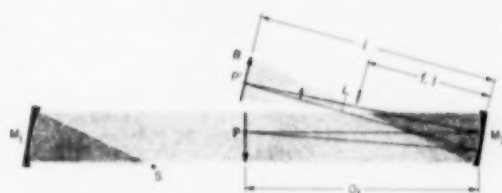
To determine camera requirements one can consider that the model is diffusely illuminated and that the schlieren light source is turned off. An image of the test section will then be created at B as determined by the focal length of M_2 and the object distance O_1. O_1 must, of course, be greater than the focal length of M_2 to create a real image and, due to space limitations, O_1 is usually on the order of twice the focal length of M_2. For a set up of this type, where the object and image distances are nearly equal, the magnification is approximately unity and the image at B will be too large for practical camera application. To reduce the image size a camera lens can be introduced at L with a focal length chosen to provide the magnification desired. The camera lens should intercept the entire bundle of light leaving the knife edge. The real image at B then serves as a virtual object to the camera at L. Thus, if a standard camera is used, the lens mount will have to be modified to permit focussing closer than the infinity focus position since the object is virtual. Rather than modify the lens mount to do this a supplemental negative lens can be used with the standard camera lens to modify the focussing range. A distinct advantage of the schlieren system is that it permits the location of the camera lens to intercept all the "useful light" of the system and permits choice of any type of camera and wide range of magnifications. A typical schlieren photograph is shown in Figure eight.

An important element in any schlieren system is the light source. The ideal schlieren light source would be
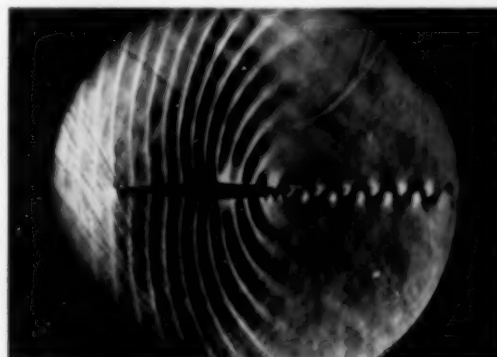

Fig. 8. Typical schlieren photograph.

Fig. 9. Self-synchronizing schlieren photograph produced by two superimposed schlieren systems.

an infinitesimally small point of infinite intensity that could be operated continuously, stroboscopically or flashed at short duration. Practically, the most satisfactory source has been the high-pressure mercury arc which has a "burning area" of 25mm length by 2mm diameter. The mercury arc has an intrinsic brilliance of 30,000 candles per square cm. It can be operated continuously or flashed at durations as low as 5 microseconds and can be operated stroboscopically as high as 100,000 flashes per second.

Self-synchronizing Stroboscopic Schlieren

The ability to operate the lamp at high rates permitted the development of a self-synchronizing stroboscopic schlieren for viewing fluctuating flow patterns. Figure nine shows a typical photograph taken with this system showing vortex discharge from the rear of a blunt airfoil. The discharge frequency is irregular in the range of 6800 cycles per second. In conventional schlieren, the phenomenon could not be seen; on conventional stroboscopic operation it could momentarily be seen, but due to frequency irregularity could not be held on the view screen. The self-stroboscopic system holds the phenomenon stationary. Essentially, it consists of two superimposed schlieren systems. One system observes intensity variations in a small area of the flow field and these intensity variations are used to control the flashing rate of the light source of the second system which is the only one viewed. Further details of the self-synchronizing stroboscope may be found in reference 4.
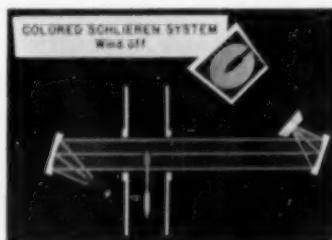
Fig. 10. Principle of the color schlieren system in which the conventional light source is replaced by a continuous spectrum.

Color Schlieren Photographs

Recently, considerable attention has been given to the color schlieren system which is merely a modification of the conventional system. However, in addition to permitting very striking schlieren photography, the color schlieren photographs are more easily interpreted since discrimination of variations in color are more easily interpreted than variation of shades of gray.

The principle is comparatively simple. As shown in Figure ten, if the conventional schlieren light source is replaced with a continuous spectrum, an image of the spectrum will be formed at the knife-edge position. Then, if the knife edge is replaced by a slit with an opening to pass one color of the spectrum, a uniform monochromatic image of the schlieren field will appear on the camera screen. By adjusting the slit to the "middle color" of the spectrum the system becomes color sensi-
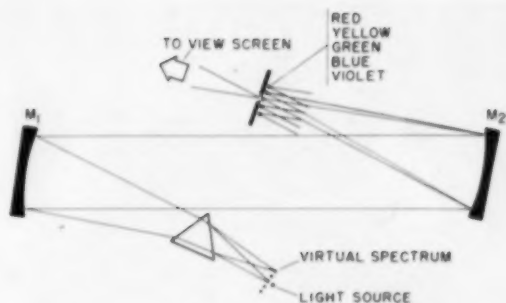
Fig. 11. Prism type color schlieren arrangement with the undisturbed green band focused on the slit opening.

tive to both direction and magnitude of the gradients in the field of the disturbance.

As shown in Figure eleven, the gradient direction is determined by the color groups [(green to red) and (green to violet)]. The strength of the disturbance is then indicated by the amount of deviation required to deflect any color from its undisturbed position to the slit opening at the green middle color.

There are several methods of introducing color into the schlieren system. The simplest method is to place a prism between the light source and collimating mirror. The single source then becomes a virtual spectrum which is re-imaged at the slit. Another method of introducing color consists of modifying the knife-edge assembly by replacing the knife edge with a transparent color grid. In this system any ray deviated from the "middle color" will appear on the screen in color corresponding to that portion of the grid through which it has passed. This has proved the most practical system for work at Ames since very little modification of the existing schlieren systems is required to permit choice of black and white or color. The color grids are prepared on 35mm Kodachrome by photographing a back illuminated slit through selected filters. The illuminated slit is mounted such that it can be translated in increments of its own width. The filters are selected to provide a grid of five colors which complement the H-6 standard schlieren light source. The H-6 lamp, being a high-pressure mercury lamp, is predominant in the blue-green region and deficient in red. The sclieren colors are not as pure as obtained from the prism, but are equally as useful for analyzing schlieren photographs.

References

1. Melton, Ben S., Prescott, Rochell and Grayhard, Everett L.: A Working Manual for Spark Shadowgraph Photography. Johns Hopkins University, Applied Physics Lab., Bumblebee Report 90, December, 1948.

2. Stevens, Victor I., Jr.: Hypersonic Research Facilities at Ames Aeronautical Laboratory, Journal Applied Physics, Vol. 21, No. 11, 1950, pp. 1150-1155 (Shadowgraph and Chronograph).

3. Schardin, Hubert, Toepler's Sriation Method. Principles for Its Application and Quantitative Evaluation. Air Ministry, AMT 249, R.T.P. translation 249 (Schlieren).

4. Lawrence, Leslie F., Schmidt, Stanley F., and Looschen, Floyd W.: A Self-Synchronizing Stroboscopic Schlieren System for the Study of Unsteady Air Flows, NACA TN 2509, October 1951.